

## Gasoline Additive for Direct Injection Gasoline Engine

This invention relates to gasoline additives and more particularly to gasoline additives having excellent solubility in gasoline and detergency in combustion chambers particularly of direct injection gasoline engines. This invention relates to gasoline compositions containing such additives.

From the view point of resource-savings and suppression of global warming, it has been a world-wide demand that the use of fossil fuels be reduced. In connection with this, an improvement in fuel consumption becomes the most important issue for gasoline-engine automobiles. On the other hand, some urban areas fail to meet environmental standards in terms of the amount of pollutants such as NO<sub>x</sub> (nitrogen oxide), and gasoline-engine automobiles are thus required to have reduced emissions of such pollutants. Direct injection gasoline engines are now considered to be the most effective means for meeting or satisfying such demands or standards.

Conventional gasoline engines are designed to form a homogeneous pre-mixture of gasoline and air by injecting gasoline into the intake port. In contrast, direct injection gasoline engines are designed to inject gasoline directly into the combustion chamber, so that they are able to form a stratified fuel mixture which is rich in the vicinity of the spark plug but highly lean elsewhere in the combustion chamber. Owing to the formation of such a stratified fuel mixture, combustion with the highly lean mixture can be achieved, leading to an improvement in fuel consumption equivalent to that of diesel engines.

Moreover, the direct injection of gasoline into the combustion chamber is contributive to the freedom from delay in gasoline vaporization as seen in conventional engines, and enables further enhanced accuracy in control of fuel injection rate.

However, direct injection gasoline engines can encounter some unexpected problems which are different from those of conventional engines due to the direct injection of gasoline into the combustion chamber. One of the problems is related to deposits formed in the combustion chamber, particularly the cavity or recess formed on the upper surface of the pistons. The stratified combustion characterizing the direct injection gasoline engine is conducted by injecting fuel into the cavity while the piston is in upward stroke, and forming a rich fuel mixture in the vicinity of the spark plug with the rebounded fuel. If deposits are formed in the cavity during combustion, the ratio of air to fuel becomes unstable because a portion of the injected fuel is absorbed by the deposits. As a result, the amount of fuel around the spark plug is decreased, and the piston is delayed in reaching the top position of the cycle. Therefore, this problem causes an adverse affect on the drivability of automobiles, the deterioration of the exhaust gas, and the generation of smoke.

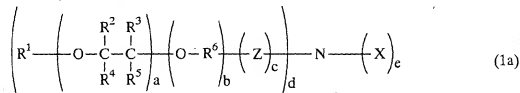
In view of the current situations, the present invention is intended to provide a gasoline additive which comprises a special nitrogen-containing compound having an excellent detergency in the combustion chamber, particularly in a recess or cavity formed on the upper surface of the piston of a direct injection gasoline chamber.

#### BRIEF SUMMARY OF THE INVENTION

After intensive research efforts made to solve the foregoing problems, it is found that nitrogen-containing compounds having specific structures are superior in detergency in a combustion chamber, particularly in cavities or

recesses formed on the upper surface of the pistons of a direct injection gasoline engine.

According to one embodiment of the present invention, there is provided a gasoline additive which comprises a nitrogen-containing compound represented by the formula



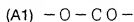
wherein R<sup>1</sup> is hydrogen or a hydrocarbon group having 1 to 30 carbon atoms, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup> and R<sup>5</sup> are each independently hydrogen, a hydrocarbon group having 1 to 16 carbon atoms, or a group represented by formula (2a) below, a is an integer of 1 to 200, R<sup>6</sup> is a hydrocarbon group having 1 to 10 carbon atoms, b is 0 or 1, Z is a group selected from Group A below, c is 0 or 1, X is a group selected from Group B below, d is an integer of 1 to 3, e is an integer of 0 to 2 and d + e = 3.

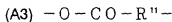
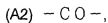
Formula (2a) is represented by



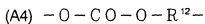
wherein R<sup>7</sup> and R<sup>8</sup> are each independently hydrogen, a hydrocarbon group having 1 to 10 carbon atoms, or an alkoxyalkyl group having 2 to 10 carbon atoms, R<sup>9</sup> is an alkylene group having 2 to 6 carbon atoms or an alkylene group having an alkoxyalkyl substituent and a total of 4 to 10 carbon atoms, R<sup>10</sup> is hydrogen or a hydrocarbon group having 1 to 30 carbon atoms, and f is an integer of 0 to 50.

Group A is constituted as follows:

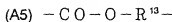




wherein  $\text{R}^{11}$  is an alkylene group having 1 to 6 carbon atoms,



wherein  $\text{R}^{12}$  is an alkylene group having 1 to 6 carbon atoms,



wherein  $\text{R}^{13}$  is an alkylene group having 1 to 6 carbon atoms; and

Group B is constituted as follows:

(B1) hydrogen,

(B2) a hydrocarbon group having 1 to 30 carbon atoms,

(B3) an alkanol group represented by the formula



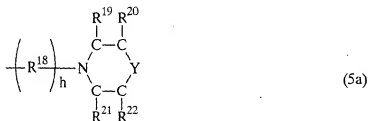
wherein  $\text{R}^{14}$  is an alkylene group having 1 to 6 carbon atoms,

(B4) a nitrogen-containing group represented by the formula



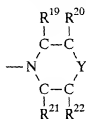
wherein  $\text{R}^{15}$  is an alkylene group having 2 to 6 carbon atoms,  $\text{R}^{16}$  is one of a hydrogen, an alkyl group having 1 to 4 carbon atoms, and a group of formula (3a),  $\text{R}^{17}$  is one of a hydrogen, a hydrocarbon group having 1 to 30 carbon atoms, and a group of formula (3a), and  $g$  is an integer of 1 to 5, and

(B5) a group represented by the formula



wherein  $R^{18}$  is an alkylene group having 2 to 6 carbon atoms,  $R^{19}$ ,  $R^{20}$ ,  $R^{21}$  and  $R^{22}$  are each independently hydrogen, a hydrocarbon group having 1 to 10 carbon atoms, or a hydroxyl group, Y is a methylene group, a methylene group substituted by either a hydrocarbon group having 1 to 10 carbon atoms or a hydroxyl group, an imino group, an imino group substituted by either a hydrocarbon group having 1 to 10 carbon atoms or hydroxyl group, or oxygen, h is 1 if e is equal to 1 and 0 or 1 if e is equal to 2 with the proviso that the group  $-N-(X)_e$  in formula (1a) is replaced by a group represented by formula (5a') below if  $h = 0$ ;

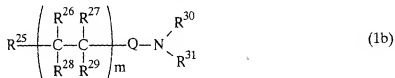
said formula (5a') being represented by



wherein the N corresponds to the N in formula (1a)

and  $R^{19} - R^{22}$  and Y are as defined in formula (5a).

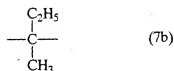
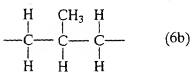
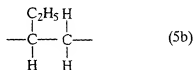
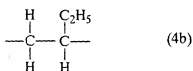
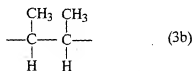
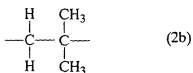
The other gasoline additive according to the present invention is a polybutenylamine compound. This compound may be those obtained by modifying the terminals of polybutene derived from the polymerization of an amine with one or more  $C_4$  hydrocarbons selected from n-butene, 2-butene and isobutene. Such compounds may be those represented by the formula



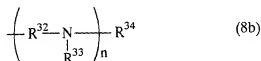
wherein  $R^{25}$  is n-butyl, sec-butyl or tert-butyl group,  $R^{26}$ ,  $R^{27}$ ,  $R^{28}$  and  $R^{29}$  are each independently a hydrogen atom, a methyl group, or an ethyl group, and are

selected such that the total carbon number of  $R^{26}$ ,  $R^{27}$ ,  $R^{28}$  and  $R^{29}$  is 2, Q is a group represented by formulae (2b) to (7b) below,  $R^{30}$  and  $R^{31}$  are each independently a hydrogen atom, a hydrocarbon group having 1 to 10 carbon atoms, an alkanol group having 1 to 8 carbon atoms or a group represented by formula (8b) below and m is an integer of 1 to 100.

Formulae (2b) to (7b) are represented by



Formula (8b) is represented by



wherein  $R^{32}$  is an alkylene group having 1 to 4 carbon atoms,  $R^{33}$  is either a hydrogen or an alkyl group having 1 to 4 carbon atoms,  $R^{34}$  is either a hydrogen or a hydrocarbon group having 1 to 10 carbon atoms, and n is an integer of 1 to 5.

#### DETAILED DESCRIPTION OF THE INVENTION

In formula (1a) representing a nitrogen-containing compound according to the first embodiment of the present invention,  $R^1$  may be hydrogen or a  $C_1 - C_{30}$  straight or branched hydrocarbon group but is preferably hydrogen, a  $C_1 -$

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Preferred alkenyl groups for R<sup>1</sup> are vinyl, propenyl, isopropenyl, straight or branched butenyl, butadienyl, straight or branched pentenyl, straight or branched hexenyl, straight or branched heptenyl, straight or branched octenyl, straight or branched nonenyl, straight or branched decenyl, straight or branched undecenyl, straight or branched dodecenyl, straight or branched tridecenyl, straight or branched tetradecenyl, straight or branched pentadecenyl, straight or branched hexadecenyl, straight or branched heptadecenyl, straight or branched octadecenyl such as oleyl, straight or branched nonadecenyl, straight or branched eicosenyl, straight or branched heneicosenyl, straight or branched docosenyl, straight or branched tricosenyl and straight or branched tetracosenyl.

- 7 -

[illegible]



(inclusive of all positional isomers) and straight or branched propylethylmethylcycloheptyl (inclusive of all positional isomers).

Preferred aryl groups for  $R^1$  are phenyl and naphthyl groups and preferred alkylaryl groups are tolyl (inclusive of all positional isomers), xylol (inclusive of all positional isomers), ethylphenyl (inclusive of all positional isomers), straight or branched propylphenyl (inclusive of all positional isomers), ethylmethylphenyl (inclusive of all positional isomers), trimethylphenyl (inclusive of all positional isomers), straight or branched butylphenyl (inclusive of all positional isomers), straight or branched propylmethylphenyl (inclusive of all positional isomers), diethylphenyl (inclusive of all positional isomers), ethyldimethylphenyl (inclusive of all positional isomers), tetramethylphenyl (inclusive of all isomers), straight or branched pentylphenyl (inclusive of all positional isomers), straight or branched hexylphenyl (inclusive of all positional isomers), straight or branched heptylphenyl (inclusive of all positional isomers), straight or branched octylphenyl (inclusive of all positional isomers), straight or branched nonylphenyl (inclusive of all positional isomers), straight or branched decylphenyl (inclusive of all positional isomers), straight or branched undecylphenyl (inclusive of all positional isomers) and straight or branched dodecylphenyl (inclusive of all positional isomers). Preferred arylalkyl groups are benzyl, methylbenzyl (inclusive of all positional isomers), dimethylbenzyl (inclusive of all positional isomers), phenethyl, methylphenethyl (inclusive of all positional isomers) and dimethylphenethyl (inclusive of all positional isomers).

Among these, preferred for  $R^1$  are hydrogen, a  $C_1 - C_{12}$  straight or branched alkyl group and a  $C_6 - C_{18}$  aryl group or alkylaryl group, more preferred are hydrogen, a  $C_1 - C_6$  straight or branched alkyl group, phenyl group and a  $C_7 - C_{15}$  straight or branched alkylaryl group, and the most preferred is hydrogen.

$R^2$ ,  $R^3$ ,  $R^4$  and  $R^5$  in formula (1a) are each independently hydrogen, a  $C_1$ ,

—  $C_{16}$  hydrocarbon group or a group represented by formula (2a) given above.

The  $C_1 - C_{16}$  hydrocarbon group used herein encompasses a  $C_1 - C_{16}$  straight or branched alkyl group, a  $C_2 - C_{16}$  straight or branched alkenyl group, a  $C_5 - C_{16}$  cycloalkyl or alkylcycloalkyl group, a  $C_6 - C_{16}$  aryl or alkylaryl group and a  $C_7 - C_{16}$  arylalkyl group.

Preferred alkyl groups are methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, straight or branched pentyl, straight or branched hexyl, straight or branched heptyl, straight or branched octyl, straight or branched nonyl, and straight or branched decyl, straight or branched undecyl, straight or branched dodecyl, straight or branched tridecyl, straight or branched tetradecyl, straight or branched pentadecyl and straight or branched hexadecyl, and preferred alkenyl groups are vinyl, propenyl, isopropenyl, straight or branched butenyl, butadienyl, straight or branched pentenyl, straight or branched hexenyl, straight or branched heptenyl, straight or branched octenyl, straight or branched nonenyl, straight or branched decenyl, straight or branched undecenyl, straight or branched dodecenyl, straight or branched tridecenyl, straight or branched tetradecenyl, straight or branched pentadecenyl and straight or branched hexadecenyl groups.

Preferred cycloalkyl groups are cyclopentyl, cyclohexyl and cycloheptyl groups, and preferred alkylcycloalkyl group are methylcyclopentyl (inclusive of all positional isomers), dimethylcyclopentyl (inclusive of all positional isomers), ethylcyclopentyl (inclusive of all positional isomers), straight or branched propylcyclopentyl (inclusive of all positional isomers), ethylmethylcyclopentyl (inclusive of all positional isomers), trimethylcyclopentyl (inclusive of all positional isomers), diethylcyclopentyl (inclusive of all positional isomers), ethyldimethylcyclopentyl (inclusive of all positional isomers), straight or branched propylmethylcyclopentyl (inclusive of all positional isomers), straight or

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Among these  $C_1 - C_{16}$  hydrocarbon groups, more preferred are  $C_1 - C_8$

straight or branched alkyl groups, the most preferred are  $C_1 - C_3$  straight or branched alkyl groups.

However, if the polar group containing a nitrogen atom is high in polarity, a nitrogen-containing compound of formula (1a) has preferably at least one  $C_8 - C_{16}$  hydrocarbon group per molecule.

$R^2$ ,  $R^3$ ,  $R^4$  and  $R^5$  in formula (1a) may be a group represented by formula (2a). In formula (2a),  $R^7$  and  $R^8$  are each independently hydrogen, a  $C_1 - C_{10}$  hydrocarbon group or a  $C_2 - C_{10}$  alkoxyalkyl group. The  $C_1 - C_{10}$  hydrocarbon group used herein encompasses a  $C_1 - C_{10}$  straight or branched alkyl group, a  $C_2 - C_{10}$  straight or branched alkenyl group, a  $C_5 - C_{10}$  cycloalkyl or alkylcycloalkyl group, a  $C_6 - C_{10}$  aryl or alkylaryl and a  $C_7 - C_{10}$  arylalkyl group.

Preferred alkyl groups are methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, straight or branched pentyl, straight or branched hexyl, straight or branched heptyl, straight or branched octyl, straight or branched nonyl and straight or branched decyl groups. Preferred alkenyl groups are vinyl, propenyl, isopropenyl, straight or branched butenyl, butadienyl, straight or branched pentenyl, straight or branched hexenyl, straight or branched heptenyl, straight or branched octenyl, straight or branched nonenyl and straight or branched decenyl groups.

Preferred cycloalkyl groups are cyclopentyl, cyclohexyl and cycloheptyl groups and preferred alkylcycloalkyl group are methylcyclopentyl (inclusive of all positional isomers), dimethylcyclopentyl (inclusive of all positional isomers), ethylcyclopentyl (inclusive of all positional isomers), straight or branched propylcyclopentyl (inclusive of all positional isomers), ethylmethylcyclopentyl (inclusive of all positional isomers), trimethylcyclopentyl (inclusive of all positional isomers), diethylcyclopentyl (inclusive of all positional isomers), ethyldimethylcyclopentyl (inclusive of all positional isomers), straight or

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- 13 -

positional isomers) and dimethylphenethyl groups (inclusive of all positional isomers).

The  $C_2 - C_{10}$  alkoxyalkyl group may be methoxymethyl, ethoxymethyl, n-propoxymethyl, isopropoxymethyl, n-butoxymethyl, isobutoxymethyl, sec-butoxymethyl, ter-butoxymethyl, pentoxymethyl (inclusive of all isomers), hexoxymethyl (inclusive of all isomers), heptoxymethyl (inclusive of all isomers), octoxymethyl (inclusive of all isomers), nonyloxymethyl (inclusive of all isomers), methoxyethyl (inclusive of all isomers), ethoxyethyl (inclusive of all isomers), propoxyethyl (inclusive of all isomers), butoxyethyl (inclusive of all isomers), pentoxyethyl (inclusive of all isomers), hexoxyethyl (inclusive of all isomers), heptoxyethyl (inclusive of all isomers), octoxyethyl (inclusive of all isomers), methoxypropyl (inclusive of all isomers), ethoxypropyl (inclusive of all isomers), propoxypropyl (inclusive of all isomers), butoxypropyl (inclusive of all isomers), pentoxypropyl (inclusive of all isomers), hexoxypropyl (inclusive of all isomers), heptoxypropyl (inclusive of all isomers), methoxybutyl (inclusive of all isomers), ethoxybutyl (inclusive of all isomers), propoxybutyl (inclusive of all isomers), butoxybutyl (inclusive of all isomers), pentoxybutyl (inclusive of all isomers), hexoxybutyl (inclusive of all isomers), methoxypentyl (inclusive of all isomers), ethoxypentyl (inclusive of all isomers), propoxypentyl (inclusive of all isomers), butoxypentyl (inclusive of all isomers), pentoxyhexyl (inclusive of all isomers), ethoxyhexyl (inclusive of all isomers), propoxyhexyl (inclusive of all isomers), butoxyhexyl (inclusive of all isomers), methoxyheptyl (inclusive of all isomers), ethoxyheptyl (inclusive of all isomers), propoxyheptyl (inclusive of all isomers), methoxyoctyl (inclusive of all isomers), ethoxyoctyl (inclusive of all isomers) and methoxynonyl groups (inclusive of all isomers).

Preferably,  $R^7$  and  $R^8$  are either both or independently hydrogen, a  $C_1 -$

C<sub>6</sub> alkyl group or a C<sub>2</sub> – C<sub>8</sub> alkoxyalkyl group, and more preferably, hydrogen or a C<sub>1</sub> – C<sub>3</sub> alkyl group.

R<sup>9</sup> in formula (2a) may be a C<sub>2</sub> – C<sub>8</sub> alkylene group or an alkylene group having an alkoxyalkylene substituent and a total of 4 to 10 carbon atoms. The C<sub>2</sub> – C<sub>8</sub> alkylene group used herein may be ethylene, propylene (1-methylethylene, 2-methylethylene), trimethylene, butylene (1-ethylethylene, 2-ethylethylene), 1,2-dimethylethylene, 2,2-dimethylethylene, 1-methyltrimethylene, 2-methyltrimethylene, 3-methyltrimethylene, tetramethylene, pentylene (1-butylethylene, 2-butylethylene), 1-ethyl-1-methylethylene, 1-ethyl-2-methylethylene, 1,1,2-trimethylethylene, 1,2,2-trimethylethylene, 1-ethyltrimethylene, 2-ethyltrimethylene, 3-ethyltrimethylene, 1,1-dimethyltrimethylene, 1,2-dimethyltrimethylene, 1,3-dimethyltrimethylene, 2,3-dimethyltrimethylene, 3,3-dimethyltrimethylene, 1-methyltetramethylene, 2-methyltetramethylene, 3-methyltetramethylene, 4-methyltetramethylene, pentamethylene, hexylenes (1-butylethylene, 2-butylethylene), 1-methyl-1-propylethylene, 1-methyl-2-propylethylene, 2-methyl-2-propylethylene, 1,1-diethylethylene, 1, 2-diethylethylene, 2,2-diethylethylene, 1-ethyl-1,2-dimethylethylene, 1-ethyl-2,2-dimethylethylene, 2-ethyl-1,1-dimethylethylene, 2-ethyl-1,2-dimethylethylene, 1,1,2,2-tetramethylethylene, 1-propyltrimethylene, 2-propyltrimethylene, 3-propyltrimethylene, 1-ethyl-1-methyltrimethylene, 1-ethyl-2-methyltrimethylene, 1-ethyl-3-methyltrimethylene, 2-ethyl-1-methyltrimethylene, 2-ethyl-2-methyltrimethylene, 2-ethyl-3-methyltrimethylene, 3-ethyl-1-methyltrimethylene, 3-ethyl-2-methyltrimethylene, 3-ethyl-3-methyltrimethylene, 1,1,2-trimethyltrimethylene, 1,1,3-trimethyltrimethylene, 1,2,2-trimethyltrimethylene, 1,2,3-trimethyltrimethylene,

1,3,3-trimethyltrimethylene, 2,2,3-trimethyltrimethylene,  
 2,3,3-trimethyltrimethylene, 1-ethyltetramethylene, 2-ethyltetramethylene,  
 3-ethyltetramethylene, 4-ethyltetramethylene, 1,1-dimethyltetramethylene,  
 1,2-dimethyltetramethylene, 1,3-dimethyltetramethylene,  
 1,4-dimethyltetramethylene, 2,2-dimethyltetramethylene,  
 2,3-dimethyltetramethylene, 2,4-dimethyltetramethylene,  
 3,3-dimethyltetramethylene, 3,4-dimethyltetramethylene,  
 4,4-dimethyltetramethylene, 1-methylpentamethylene, 2-methylpentamethylene,  
 3-methylpentamethylene, 4-methylpentamethylene, 5-methylpentamethylene  
 and hexamethylene groups.

The alkylene group having an alkoxyalkylene substituent and a total of 4 to 10 carbon atoms may be an alkoxyalkylene-substituted ethylene group having a total of 2 to 8 carbon atoms, such as 1- (methoxymethyl) ethylene, 2-(methoxymethyl)ethylene, 1-(methoxyethyl)ethylene, 2-(methoxyethyl)ethylene, 1-(ethoxymethyl)ethylene, 2-(ethoxyethyl)ethylene, 1-methoxymethyl-2-methylethylene, 1,1-bis(methoxymethyl)ethylene, 2,2-bis(methoxymethyl)ethylene, 1,2-bis(methoxymethyl)ethylene, 1,1-bis(methoxyethyl)ethylene, 2,2-bis(methoxyethyl)ethylene, 1,2-bis(methoxyethyl)ethylene, 1,1-bis(ethoxymethyl)ethylene, 2,2-bis(ethoxymethyl)ethylene, 1,2-bis(ethoxymethyl)ethylene, 1-methyl-2-methoxymethylethylene, 1-methoxymethyl-2-methylethylene, 1-ethyl-2-methoxymethylethylene, 1-methoxymethyl-2-ethylethylene, 1-methyl-2-ethoxymethylethylene, 1-ethoxymethyl-2-methylethylene, 1-ethyl-2-ethoxymethylethylene, 1-ethoxymethyl-2-ethylethylene, 1-methyl-2-methoxyethylethylene, 1-methoxyethyl-2-methylethylene, 1-ethyl-2-methoxyethylethylene and 1-methoxyethyl-2-ethylethylene groups.

Particularly preferred for R<sup>9</sup> are either C<sub>2</sub> - C<sub>4</sub> alkylene groups or



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f in formula (2a) is an integer optionally selected from the range of 0 to 50, but is an integer of preferably 0 to 30, more preferably 0 to 20.

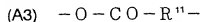
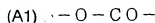
The group of formula (2a) is preferably one in which  $R^7$  and  $R^8$  are each independently hydrogen, a  $C_1 - C_6$  alkyl group or a  $C_2 - C_6$  alkoxyalkyl group,  $R^9$  is a  $C_2 - C_6$  alkylene group or an alkoxyalkylene-substituted ethylene group having a total of 2 to 8 carbon atoms,  $R^{10}$  is a  $C_1 - C_{24}$  alkyl group, and  $f$  is an integer of 0 to 30. This group of formula (2a) may be conveniently hereinafter called a "preferred substituent (PF1)". The group of formula (2a) is more preferably one in which  $R^7$  and  $R^8$  are each independently hydrogen or a  $C_1 - C_3$  alkyl group,  $R^9$  is a  $C_2 - C_4$  alkylene group,  $R^{10}$  is a  $C_1 - C_{12}$  alkyl group, and  $f$  is an integer of 0 to 20. This group of formula (2a) may also be conveniently hereinafter called a "more preferred substituent (PF2)".

The nitrogen-containing compounds according to the present invention are preferably those of formula (1a) in which R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup> and R<sup>5</sup> are hydrogen, a C<sub>1</sub> – C<sub>8</sub> alkyl group or a “preferred substituent (PF1)”, more preferably those of formula (1a) in which R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup> and R<sup>5</sup> are hydrogen, a C<sub>1</sub> – C<sub>8</sub> alkyl group or a “more preferred substituent (PF2)”.

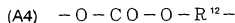
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3-methyltrimethylene, tetramethylene, 1-methyltetramethylene, 2-methyltetramethylene, 3-methyltetramethylene, 4-methyltetramethylene, pentamethylene, 1-methylpentamethylene, 2-methylpentamethylene, 3-methylpentamethylene, 4-methylpentamethylene, 5-methylpentamethylene and hexamethylene groups.

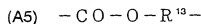
Z in formula (1a) is a group selected from Group A. Group A consists of :



wherein  $R^{11}$  is a  $C_1 - C_6$  alkylene group



wherein  $R^{12}$  is a  $C_1 - C_6$  alkylene group



wherein  $R^{13}$  is a  $C_1 - C_6$  alkylene group.

$R^{11}$ ,  $R^{12}$  and  $R^{13}$  are each a  $C_1 - C_6$  alkylene group. Specific examples of the alkylene group are methylene, ethylene, propylene (1-methylethylene, 2-methylethylene), trimethylene, butylene (1-ethylethylene, 2-ethylethylene), 1,2-dimethylethylene, 2,2-dimethylethylene, 1-methyltrimethylene, 2-methyltrimethylene, 3-methyltrimethylene, tetramethylene, pentylene (1-butylethylene, 2-butylethylene), 1-ethyl-1-methylethylene, 1-ethyl-2-methylethylene, 1,1,2-trimethylethylene, 1,2,2-trimethylethylene, 1-ethyltrimethylene, 2-ethyltrimethylene, 3-ethyltrimethylene, 1,1-dimethyltrimethylene, 1,2-dimethyltrimethylene, 1,3-dimethyltrimethylene, 2,3-dimethyltrimethylene, 3,3-dimethyltrimethylene, 1-methyltetramethylene, 2-methyltetramethylene, 3-methyltetramethylene, 4-methyltetramethylene, pentamethylene, hexylene (1-butylethylene, 2-butylethylene),

1-methyl-1-propylethylene, 1-methyl-2-propylethylene,  
2-methyl-2-propylethylene, 1,1-diethylethylene, 1,2-diethylethylene,  
2,2-diethylethylene, 1-ethyl-1,2-dimethylethylene, 1-ethyl-2,2-dimethylethylene,  
2-ethyl-1,1-dimethylethylene, 2-ethyl-1,2-dimethylethylene,  
1,1,2,2-tetramethylethylene, 1-propyltrimethylene, 2-propyltrimethylene,  
3-propyltrimethylene, 1-ethyl-1-methyltrimethylene, 1-ethyl-2-methyltrimethylene,  
1-ethyl-3-methyltrimethylene, 2-ethyl-1-methyltrimethylene,  
2-ethyl-2-methyltrimethylene, 2-ethyl-3-methyltrimethylene,  
3-ethyl-1-methyltrimethylene, 3-ethyl-2-methyltrimethylene,  
3-ethyl-3-methyltrimethylene, 1,1,2-trimethyltrimethylene,  
1,1,3-trimethyltrimethylene, 1,2,2-trimethyltrimethylene,  
1,2,3-trimethyltrimethylene, 1,3,3-trimethyltrimethylene,  
2,2,3-trimethyltrimethylene, 2,3,3-trimethyltrimethylene, 1-ethyltetramethylene,  
2-ethyltetramethylene, 3-ethyltetramethylene, 4-ethyltetramethylene,  
1,1-dimethyltetramethylene, 1,2-dimethyltetramethylene,  
1,3-dimethyltetramethylene, 1,4-dimethyltetramethylene,  
2,2-dimethyltetramethylene, 2,3-dimethyltetramethylene,  
2,4-dimethyltetramethylene, 3,3-dimethyltetramethylene,  
3,4-dimethyltetramethylene, 4,4-dimethyltetramethylene,  
1-methylpentamethylene, 2-methylpentamethylene, 3-methylpentamethylene,  
4-methylpentamethylene, 5-methylpentamethylene and hexamethylene groups.

- 19 -

propylene (1-methylethylene, 2-methylethylene) and trimethylene groups.

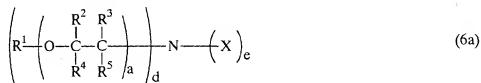
Among Group A, Z is preferably (A1), (A2) or (A4).

In formula (1a) representing the inventive nitrogen-containing compound, a is an integer of between 1 and 200, preferably 2 and 100.

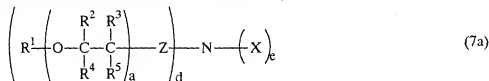
In formula (1a), b and c are each 0 or 1.

If b is 0 and c is 0, the compound of formula (1a) is represented by formula (6a) below. If b is 0 and c is 1, the compound of formula (1a) is represented by formula (7a) below. If b is 1 and c is 0, the compound of formula (1a) is represented by formula (8a) below. If both b and c are 1, the compound of formula (1a) is represented by formula (9a).

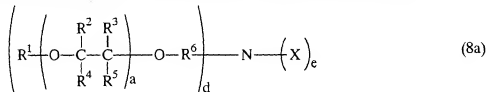
Formulae (6a) - (9a) are represented by



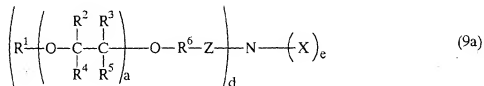
wherein R<sup>1</sup> through R<sup>5</sup>, X, a, d and e are as defined in formula (1a).



wherein R<sup>1</sup> through R<sup>5</sup>, X, Z, a, d and e are as defined in formula (1a).



wherein R<sup>1</sup> through R<sup>6</sup>, X, a, d and e are as defined in formula (1a).

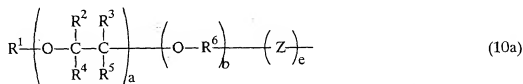


wherein R<sup>6</sup> through R<sup>9</sup>, X, Z, a, d and e are as defined in formula (1a).

c in formula (1a) may be 0 or 1, but is preferably 0.

In formula (1a), d is an integer from 1 to 3, preferably 1 or 2, and e is an integer from 0 to 2, preferably 1 or 2, the sum of d and e is equal to 3, most preferably, d is equal to 1 when e is equal to 2.

In formula (1a), if d is equal to 2, the inventive nitrogen-containing compound has two groups represented by formula (10a) below per molecule

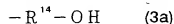


wherein R<sup>1</sup> through R<sup>6</sup>, Z, a, b and c are as defined in formula (1a).

In formula (1a) representing the inventive nitrogen-containing compound, X is a group selected from Group B below:

#### Group B

- (B1) hydrogen
- (B2) a C<sub>1</sub> - C<sub>30</sub> hydrocarbon group
- (B3) an alkanol group represented by the formula



wherein R<sup>14</sup> is a C<sub>1</sub> - C<sub>6</sub> alkylene group

- (B4) a nitrogen-containing group represented by the formula



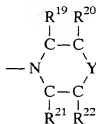
wherein R<sup>15</sup> is a C<sub>2</sub> - C<sub>6</sub> alkylene group, R<sup>16</sup> is one of a hydrogen, a C<sub>1</sub> - C<sub>4</sub> alkyl group, or a group of formula (3a), R<sup>17</sup> is one of a hydrogen, a C<sub>1</sub> - C<sub>30</sub> alkyl group, or a group of formula (3a), and g is an integer from 1 to 5, and

(B5) Group represented by the formula



wherein  $\text{R}^{18}$  is a  $\text{C}_2 - \text{C}_6$  alkylene group,  $\text{R}^{19}$ ,  $\text{R}^{20}$ ,  $\text{R}^{21}$  and  $\text{R}^{22}$  are each independently a hydrogen, or a  $\text{C}_1 - \text{C}_{30}$  hydrocarbon or a hydroxyl group, Y is one of a methylene group, a methylene group substituted by either a  $\text{C}_1 - \text{C}_{10}$  hydrocarbon or a hydroxyl group, an imino group, an imino group substituted by either a  $\text{C}_1 - \text{C}_{10}$  hydrocarbon or a hydroxyl group, and an oxygen, h is 1 if e = 1 or 0 or 1 if e = 2, with the proviso that the group  $\text{---} \text{N} \text{---} (\text{X})_e$  in formula (1a) is replaced by a group represented by formula (5a') below if h = 0;

said formula (5a') being represented by



wherein the N corresponds to the N in formula (1a) and  $\text{R}^{19} - \text{R}^{22}$  and Y are as defined in formula (5a).

The  $\text{C}_1 - \text{C}_{30}$  hydrocarbon groups for (B2) are those already identified with regard to  $\text{R}^1$  in formula (1a), such as  $\text{C}_1 - \text{C}_{24}$  straight or branched alkyl groups,  $\text{C}_2 - \text{C}_{24}$  straight or branched alkenyl groups,  $\text{C}_5 - \text{C}_{13}$  cycloalkyl or alkylcycloalkyl groups,  $\text{C}_6 - \text{C}_{18}$  aryl or alkylaryl groups and  $\text{C}_7 - \text{C}_{19}$  arylalkyl groups.

Preferred for (B2) are  $C_1 - C_{12}$  straight or branched alkyl groups,  $C_6 - C_{12}$  aryl or arylalkyl groups. The most preferred (B2) groups are  $C_1 - C_6$  straight or branched alkyl groups, phenyl groups and  $C_7 - C_9$  arylalkyl groups.

In formula (3a) representing an alkanol group (B3),  $R^{14}$  is a  $C_1 - C_6$  alkylene group such as those already exemplified with respect to  $R^{11}$ ,  $R^{12}$  and  $R^{13}$  above. Among these alkylene groups, preferred for  $R^{14}$  are  $C_1 - C_4$  alkylene groups such as methylene, ethylene, propylene (1-methylethylene, 2-methylethylene), trimethylene, butylene (1-ethylethylene, 2-ethylethylene), 1,2-dimethylethylene, 2,2-dimethylethylene, 1-methyltrimethylene, 2-methyltrimethylene, 3-methyltrimethylene and tetramethylene groups. The most preferred are  $C_1 - C_3$  alkylene groups such as methylene, ethylene, propylene (1-methylethylene, 2-methylethylene) and trimethylene groups.

In formula (4a) representing a nitrogen-containing compound (B4),  $R^{15}$  is a  $C_2 - C_6$  alkylene group such as those already exemplified with regard to  $R^9$  above.

Among these alkylene groups, preferred for  $R^{15}$  are ethylene, propylene (1-methylethylene, 2-methylethylene), trimethylene, butylene (1-ethylethylene, 2-ethylethylene), 1,2-dimethylethylene, 2,2-dimethylethylene, 1-methyltrimethylene, 2-methyltrimethylene, 3-methyltrimethylene and tetramethylene groups. The most preferred are  $C_1 - C_3$  alkylene groups such as methylene, ethylene, propylene (1-methylethylene, 2-methylethylene) and trimethylene groups.

$R^{16}$  in formula (4a) is one of a hydrogen, a  $C_1 - C_4$  alkyl group, and a group represented by formula (3a). Specific examples of the  $C_1 - C_4$  alkyl group are methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl and tert-butyl groups. Preferred are  $C_1 - C_3$  alkyl groups and more preferred are methyl and ethyl groups.

$R^{17}$  in formula (4a) is one of a hydrogen, a  $C_1 - C_{30}$  hydrocarbon group, and a group represented by formula (3a). Preferred examples of the  $C_1 - C_{30}$  hydrocarbon group here are those already identified with regard to  $R^1$ , such as  $C_1 - C_{24}$  straight or branched alkyl groups,  $C_2 - C_{24}$  straight or branched alkenyl groups,  $C_5 - C_{13}$  cycloalkyl or alkylcycloalkyl groups,  $C_6 - C_{18}$  aryl or alkylaryl groups, and  $C_7 - C_{19}$  arylalkyl groups.

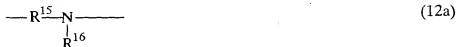
More preferred for  $R^{17}$  are a hydrogen,  $C_1 - C_{12}$  straight or branched alkyl groups,  $C_6 - C_{12}$  aryl or arylalkyl groups or the groups of formula (3a). The most preferred for  $R^{17}$  are hydrogen,  $C_1 - C_6$  straight or branched alkyl groups, phenyl groups,  $C_7 - C_9$  arylalkyl groups and the groups of formula (3a).

In formula (4a), g is an integer from 1 to 5, preferably 1 to 4, and more preferably, 1 to 3.

The group represented by the formula



is included in the group of formula (4a), wherein g is an integer from 1 to 5, preferably 1 to 4, and more preferably 1 to 3. The constituting unit (11a) is



wherein  $R^{15}$  and  $R^{16}$  are as defined in formula (4a).

Therefore, the group of formula (11a) is a group which can be comprised of constituting units of formula (12a) in the following manner:

- (i) one kind of the constituting unit of formula (12a), and
- (ii) more than one kind of random-, alternating- or block bonded constituting units of formula (12a).

The nitrogen-containing group (B4) of formula (4a) is preferably a group



in which R<sup>15</sup> is a C<sub>2</sub> – C<sub>4</sub> alkylene group, R<sup>16</sup> is one of a hydrogen, a C<sub>1</sub> – C<sub>3</sub> alkyl group, and a group of formula (3a), R<sup>17</sup> is one of a hydrogen, a C<sub>1</sub> – C<sub>12</sub> straight or branched alkyl group, a C<sub>6</sub> – C<sub>12</sub> aryl or alkylaryl group, and a group of formula (3a), and g is an integer from 1 to 4. More preferably, (B4) is a group in which R<sup>15</sup> is ethylene group, propylene group (1-methylethylene, 2-methylethylene) or trimethylene group, R<sup>16</sup> is hydrogen, methyl group, ethyl group or the group of formula (3a), R<sup>17</sup> is a hydrogen, a C<sub>1</sub> – C<sub>6</sub> straight or branched alkyl group, phenyl group, a C<sub>7</sub> – C<sub>9</sub> alkylaryl group, or a group of formula (3a), and g is an integer from 1 to 3.

In formula (5a) representing the group (B5), R<sup>18</sup> is a C<sub>2</sub> – C<sub>8</sub> alkylene group, such as those already exemplified with regard to R<sup>15</sup>. Among these alkylene groups, preferred for R<sup>18</sup> are C<sub>2</sub> – C<sub>4</sub> alkylene groups such as ethylene, propylene (1-methylethylene, 2-methylethylene), trimethylene, butylene (1-ethylethylene, 2-ethylethylene), 1,2-dimethylethylene, 2,2-dimethylethylene, 1-methyltrimethylene, 2-methyltrimethylene, 3-methyltrimethylene and tetramethylene groups. The most preferred are C<sub>2</sub> – C<sub>3</sub> alkylene groups such as methylene, ethylene, propylene (1-methylethylene, 2-methylethylene) and trimethylene groups.

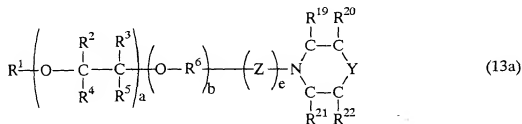
R<sup>19</sup>, R<sup>20</sup>, R<sup>21</sup> and R<sup>22</sup> in formula (5a) are each independently hydrogen, a C<sub>1</sub> – C<sub>10</sub> hydrocarbon group or a hydroxyl group. The C<sub>1</sub> – C<sub>10</sub> hydrocarbon group here encompasses those already identified with regard to R<sup>7</sup> and R<sup>8</sup>, such as C<sub>1</sub> – C<sub>10</sub> straight or branched alkyl groups, C<sub>2</sub> – C<sub>10</sub> straight or branched alkenyl groups, C<sub>5</sub> – C<sub>10</sub> cycloalkyl or alkylcycloalkyl groups, C<sub>6</sub> – C<sub>10</sub> aryl or alkylaryl groups and C<sub>7</sub> – C<sub>10</sub> arylalkyl groups.

Among these, R<sup>19</sup>, R<sup>20</sup>, R<sup>21</sup> and R<sup>22</sup> are each preferably hydrogen, a C<sub>1</sub> - C<sub>6</sub> alkyl group or a hydroxyl group, and more preferably each is a hydrogen, a C<sub>1</sub> - C<sub>3</sub> alkyl group, or a hydroxyl group.

Y in formula (5a) is a methylene group, a C<sub>1</sub> - C<sub>10</sub> hydrocarbon- or hydroxyl-substituted methylene group, an imino group, a C<sub>1</sub> - C<sub>10</sub> hydrocarbon- or hydroxyl-substituted imino group, or an oxygen. The C<sub>1</sub> - C<sub>10</sub> hydrocarbon group here encompasses those already identified with regard to R<sup>7</sup> and R<sup>8</sup>, such as C<sub>1</sub> - C<sub>10</sub> straight or branched alkyl groups, C<sub>2</sub> - C<sub>10</sub> straight or branched alkenyl groups, C<sub>5</sub> - C<sub>10</sub> cycloalkyl or alkylcycloalkyl groups, C<sub>6</sub> - C<sub>10</sub> aryl or alkylaryl groups and C<sub>7</sub> - C<sub>10</sub> arylalkyl groups, among which preferred are C<sub>1</sub> - C<sub>6</sub> alkyl groups and more preferred are C<sub>1</sub> - C<sub>3</sub> alkyl groups.

Among these, Y is preferably a methylene group, a C<sub>1</sub> - C<sub>6</sub> alkyl- or hydroxyl-substituted methylene group, an imino group, a C<sub>1</sub> - C<sub>6</sub> alkyl- or hydroxyl-substituted imino group, or oxygen. Most preferably Y is an imino group, a C<sub>1</sub> - C<sub>3</sub> alkyl- or hydroxyl-substituted imino group, or oxygen.

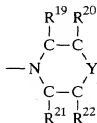
In formula (5a), h is equal to 1 if e in formula (1a) is equal to 1, and 0 or 1 if e in formula (1a) is equal to 2. However, if e is equal to 2 and h is equal to 0, N in formula (5a) corresponds to N in formula (1a). More specifically, if e is equal to 2 and h is equal to 0, N contained in the compound of formula (1a) becomes one member forming the heterocyclic ring indicated by formula (5a), as represented by the formula



wherein R<sup>1</sup> - R<sup>6</sup>, Z, a, b and c are as defined in formula (1a) and R<sup>19</sup> - R<sup>22</sup> and Y are defined in formula (5a).

The group (B5) of formula (5a) is preferably a group in which R<sup>18</sup> is a C<sub>2</sub> - C<sub>4</sub> alkylene group, R<sup>19</sup> - R<sup>22</sup> are each independently one of a hydrogen, a C<sub>1</sub> -

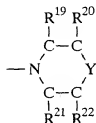
C<sub>6</sub> alkyl group, and a hydroxyl group, Y is a methylene group, a C<sub>1</sub> – C<sub>6</sub> alkyl- or hydroxyl-substituted methylene group, an imino group, a C<sub>1</sub> – C<sub>6</sub> alkyl- or hydroxyl-substituted imino group or oxygen, h is equal to 1 if e is equal to 1 and h is equal to 0 or 1 if e is equal to 2, with the proviso that N in formula (5a) corresponds to N in formula (1a) if h is equal to 0; and most preferably a group in which R<sup>18</sup> is ethylene group, propylene group (1-methylethylene group, 2-methylethylene group) or trimethylene group, R<sup>19</sup> – R<sup>22</sup> are each independently hydrogen, a C<sub>1</sub> – C<sub>3</sub> alkyl group or a hydroxyl group, Y is an imino group, a C<sub>1</sub> – C<sub>3</sub> alkyl- or hydroxyl-substituted imino group, or oxygen, h is equal to 1 if e is equal to 1 and h is equal to 0 or 1 if e is equal to 2, with proviso that the group —N—(X)<sub>e</sub> in formula (1a) is replaced by a group represented by formula (5a') below if h = 0; said formula (5a') being represented by



wherein the N corresponds to the N in formula (1a) and R<sup>19</sup> – R<sup>22</sup> and Y are as defined in formula (5a).

X is preferably (B1), (B3), (B4) or (B5).

inventive nitrogen-containing compound is described above. Preferred nitrogen-containing compounds of the present invention are those of formula (1a) in which R<sup>1</sup> is either a hydrogen, a C<sub>1</sub> – C<sub>12</sub> straight or branched alkyl group, or a C<sub>6</sub> – C<sub>18</sub> aryl or alkylaryl group; R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup> and R<sup>5</sup> are each independently

[illegible]

[illegible]
$$\begin{array}{c} \text{R}^{19} \quad \text{R}^{20} \\ | \quad | \\ -\text{N} - \text{C} - \text{C} - \text{Y} \\ | \quad | \\ \text{R}^{21} \quad \text{R}^{22} \end{array}$$

- 29 -

defined in formula (5a).

The nitrogen-containing compound of formula (1a) may be produced by any suitable method. As an example, the nitrogen-containing compound may be synthesized by the following process including (A) ketimine conversion reaction, (B) polymerization and (C) hydrolysis.

(A) Ketimine conversion reaction

A ketimine compound is produced by heating and then hydrolyzing a compound having a ketone and more than two amino groups in the molecule or a compound having a combination of at least one amino group and another group having at least one active hydrogen, such as an alkanol, an imino or a carboxyl group in the molecule.

Examples of compounds having more than two amino groups are diamines such as ethylenediamine, propylenediamine (1,2-diaminopropane) and trimethylenediamine (1,3-diaminopropane) and polyamines (more than 3 nitrogen atoms) such as diethylenetriamine, dipropylenetriamine, di(trimethylene)triamine, dimethylaminopropylenediamine, triethylenetetramine, tripropylenetetramine, tetraethylenepentamine, tetrapropylenepentamine, pentaethylenhexamine and pentapropylenhexamine.

Examples of compounds having at least one amino group and an alkanol group in the molecule are alkanolamines such as monomethanolamine, monoethanolamine, mono-n-propanolamine, monoisopropanolamine, mono(straight or branched)butanolamine (the position of hydroxyl group may vary), mono(straight or branched)pentanolamine (the position of hydroxyl group may vary), mono(straight or branched)hexanolamine (the position of hydroxyl group may vary) and 2-(2-aminoethylamino)ethanol.

Examples of compounds having an amino group and an imino group in the molecule are the above-exemplified polyamines and

4-aminomethylpiperidine.

Examples of compounds having an amino group and a carboxyl group in the molecule are amino acids such as alanine,  $\beta$ -alanine and N-(2-aminoethyl)glycine.

Eligible ketones are those represented by the formula



wherein  $\text{R}^{23}$  and  $\text{R}^{24}$  are each independently a straight or branched alkyl group having 1 to 10, preferably 1 to 5 carbon atoms.

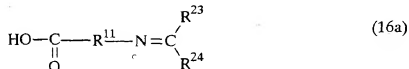
Among ketones having formula (14a), preferred are ketones having a branched alkyl group and strong steric hindrance, such as isobutylmethylketone, isobutylethylketone and diisobutylketone.

The reaction of an alkanolamine with a ketone results in a ketimine compound represented by the formula



wherein  $\text{R}^6$  is as defined in formula (1a) and  $\text{R}^{23}$  and  $\text{R}^{24}$  are as defined in formula (14a).

The reaction of an amino acid with a ketone results in a ketimine compound represented by the formula



wherein  $\text{R}^{11}$  is as defined in the formula representing the group of (A3) and  $\text{R}^{23}$  and  $\text{R}^{24}$  are as defined in formula (14a).

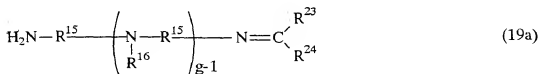
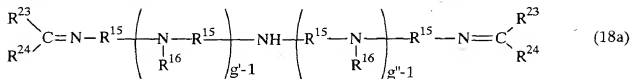
The reaction of a diamine with a ketone results in a ketimine compound

represented by the formula



wherein  $\text{R}^{15}$  is as defined in formula (4a) and  $\text{R}^{23}$  and  $\text{R}^{24}$  are as defined in formula (14a).

The reaction of a polyamine i.e. more than 3 nitrogen atoms with a ketone results in a ketimine compound represented by the formulae



wherein  $\text{R}^{15}$  and  $\text{R}^{16}$  are as defined in formula (4a), g, g' and g" are as g is defined in formula (4a), and  $\text{R}^{23}$  and  $\text{R}^{24}$  are as defined in formula (14a).

Upon the reaction of an amine used as a starting material with the ketone of formula (14a), it is preferred to react the amine with an equimolar amount of the ketone.

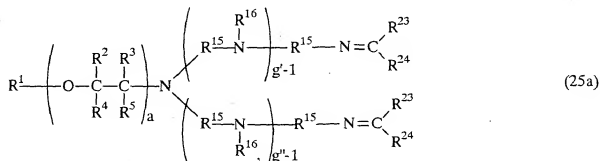
When an alkanolamine, an amino acid, or a diamine is used, they are preferably reacted with an equimolar amount of the ketone, and when a polyamine i.e. containing more than 3 nitrogen atoms is used, it is preferably reacted with either an equimolar amount of the ketone or two molar equivalents of the ketone.

The reaction for obtaining the ketimine compound is conducted at any suitable temperature, but preferably at a temperature of 40 to 180 °C, and more preferably at a temperature of 80 to 150 °C.

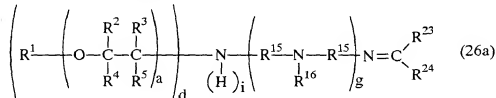




is as defined in the formula representing (A3),  $R^{15}$  is as defined in formula (4a),  $R^{23}$  and  $R^{24}$  are each as defined in formula (14a), and  $i$  is an integer to be selected such that  $d + i = 2$ .



wherein  $a$ ,  $R^1$ ,  $R^2$ ,  $R^3$ ,  $R^4$  and  $R^5$  are each as defined in formula (1a),  $R^{15}$  and  $R^{16}$  are each as defined in formula (4a), and  $g'$  and  $g''$  are the same as  $g$  in formula (4a), and  $R^{23}$  and  $R^{24}$  are as defined in formula (14a).



wherein  $a$ ,  $d$ ,  $R^1$ ,  $R^2$ ,  $R^3$ ,  $R^4$  and  $R^5$  are as defined in formula (1a) and  $g$ ,  $R^{15}$  and  $R^{16}$  are as defined in formula (4a),  $R^{23}$  and  $R^{24}$  are as defined in formula (14a), and  $i$  is an integer to be selected such that  $d + i = 2$ .

Preferred examples of the epoxy compound of formula (20a) are ethyleneoxide, propyleneoxide, isobutyleneoxide, 1,2-butyleneoxide, 2,3-butyleneoxide, trimethylethyleneoxide, tetramethylethyleneoxide, 1,2-epoxyhexane, 1,2-epoxyheptane, 1,2-epoxyoctane, 1,2-epoxydecane, 1,2-epoxydodecane, 1,2-epoxytetradecane, 1,2-epoxyhexadecane, 1,2-epoxyoctadecane, methylglycidyl ether, ethylglycidyl ether, n-propylglycidyl ether, isopropylglycidyl ether, n-butylglycidyl ether, isobutylglycidyl ether, sec-butylglycidyl ether, tert-butylglycidyl ether, straight or branched pentylglycidyl ether, straight or branched hexylglycidyl ether, straight or branched heptylglycidyl ether, straight or branched octylglycidyl ether, straight or

[illegible]

1,2-epoxy-5-(2-oxapropyl)-4,7-dioxaoctane,  
1,2-epoxy-3,5-bis(2-oxapropyl)-4,7-dioxaoctane,  
1,2-epoxy-3,6 bis(2-oxapropyl)-4,7-dioxaoctane,  
1,2-epoxy-6-methoxy-4,8-dioxanonane, 1,2-epoxy-4,7,10-trioxaundecane,  
1,2-epoxy-5-methyl-4,7,10-trioxaundecane,  
1,2-epoxy-8-methyl-4,7,10-trioxaundecane,  
4,5-epoxy-9-methyl-2,7,10-trioxaundecane,  
1,2-epoxy-6,9-dimethyl-4,7,10-trioxaundecane,  
1,2-epoxy-6,9-bis(2-oxapropyl)-4,7,10-trioxaundecane,  
1,2-epoxy-4,7,10,13-tetraoxatetradecane,  
4,5-epoxy-2,7,10,13-tetraoxatetradecane,  
7,8-epoxy-2,5,10,13-tetraoxatetradecane,  
7,8-epoxy-3,12-dimethyl-2,5,10,13-tetraoxatetradecane  
and 1,2-epoxy-6,9,12-trimethyl-4,7,10,13-tetraoxatetradecane.

Although not restricted, the ratio of the epoxy compound of formula (20a) to a ketimine compound in the polymerization reaction is preferably in the range of 5 to 100 moles per mol of the ketimine compound.

Although not restricted, the polymerization may be carried out at a temperature of 60 to 180 °C, preferably 80 to 150 °C.

(C) Hydrolysis

The above-obtained polyoxoalkylene glycol derivative having the ketimine compound at the terminal ends is heated in the presence of an excess amount of water thereby obtaining the nitrogen-containing compound of formula (1a) according to the present invention.

The reaction temperature of this process is not restricted, but is in the range of preferably 40 to 150 °C, and more preferably, 50 to 100 °C.

It is also possible to obtain a nitrogen-containing compound having an

alkanolamine group at the terminal end by adding an epoxy compound of formula (20a) to the amino group at the terminal end of the hydrolyzed polyoxyalkylene glycol derivative having the ketimine compound.

The inventive nitrogen-containing compound of formula (1a) can be obtained by performing the above polymerization (B) without performing either of the ketimine conversion reaction (A) and the hydrolysis (C) when using as the amine any of morpholine,

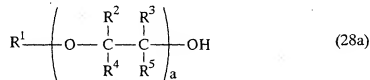
N- $\beta$ -hydroxyethylmorpholine, N-(2-hydroxypropyl)morpholine, piperidine, 1-(2-hydroxyethyl)piperidine, 2-dimethylaminoethanol, 2-dimethylamino-1-propanol, 1-dimethylamino-2-propanol, 4-dimethylamino-1-butanol, 2-dimethylamino-2-methyl-1-propanol, 2-diethylaminoethanol, 3-diethylamino-1-propanol, 1-diethylamino-2-propanol, 2-diisopropylaminoethanol, 2-dimethylaminoethylamine, 3-dimethylaminopropylamine, 2-diethylaminoethylamine, 3-diethylaminopropylamine, 2-diisopropylaminoethylamine, 1-aminopiperidine, 1-(2-aminoethyl)piperidine, 4-(2-aminoethyl)morpholine, 4-(3-aminopropyl)morpholine, piperazine, 1-methylpiperazine and 1-(2-aminoethyl)piperidine.

Alternatively, the nitrogen-containing compound of formula (1a) of the present invention may be synthesized by the following process including (D) polymerization, (E) chloroformation, and (F) carbamation.

#### (D) Polymerization

In the presence of a base such as potassium hydroxide, sodium hydroxide, or sodium alkoxide, as a catalyst, a polymerization product in the form of a metal alkoxide is produced by polymerizing the epoxy compound of formula (20a) using an oxygen-containing compound of formula (27a) below as a reaction initiator. The resulting polymerization product is neutralized with an

acid, such as hydrochloric acid thereby obtaining a polyoxyalkylene glycol derivative represented by formula (27a) below:



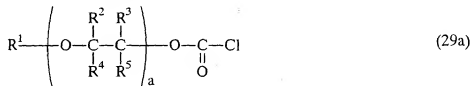
$R^1$ ,  $R^2$ ,  $R^3$ ,  $R^4$  and  $R^5$  and  $a$  in formulae (27a) and (28a) are as defined in formula (1a).

Although not restricted, the ratio of the epoxy compound of formula (20a) to the oxygen-containing compound of formula (27a) is preferably in the range of 5 to 100 moles per mole of oxygen-containing compound.

The reaction temperature of this process is selected arbitrarily, but is in the range of preferably 60 to 180 °C, more preferably 80 to 150 °C.

#### (E) Chloroformation

The polyoxyalkylene glycol derivative of formula (28a), or the metallic alkoxide thereof prior to neutralization, is subjected to chloroformation at room temperature in the presence of an excess amount of phosgene thereby obtaining a chlorine-containing compound of the formula



wherein  $R^1$ ,  $R^2$ ,  $R^3$ ,  $R^4$  and  $R^5$  are as defined in formula (1a).

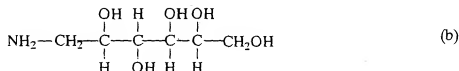
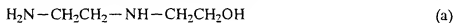
#### (F) Carbamation

The chlorine-containing compound of formula (29a) is reacted with an amine compound of formula (30a) thereby obtaining the inventive nitrogen-containing compound:



wherein X corresponds to the X of formula (1a) in which e is equal to 2, R<sup>12</sup> is as defined in the formula representing the group (A4), and j is 0 or 1.

Examples of an amine compound of formula (30a) are ethylenediamine, propylenediamine(1,2-diaminopropane), trimethylenediamine(1,3-diaminopropane), dimethylaminopropylamine, diethylenetriamine, dipropylenetriamine, di(trimethylene)toriamine, dimethylaminopropylenediamine, triethylenetetramine, tripropylenetetramine, tetraethylenepentamine, tetrapropylenepentamine, pentaethylenhexamine, pentapropylenhexamine, piperidine, 1-aminopiperidine, 4-aminomethylpiperidine, 1-(2-aminoethyl)piperidine, morpholine, 4-aminomorpholine, 4-(2-aminoethyl)morpholine, 4-(3-aminopropyl)morpholine, piperadine, 1-amino-4-methylpiperadine, 1-(2-aminoethyl)piperadine, 1-(3-aminopropyl)piperadine, monomethanolamine, monoethanolamine, mono-n-propanolamine, monoisopropanolamine, mono(straight or branched) butanolamine( the position of hydroxyl group may vary ), mono(straight or branched)pentanolamine(the position of hydroxyl group may vary ), mono(straight or branched)hexanolamine(the position of hydroxyl group may vary ), 2-(2-aminoethyl)ethanol (as represented by Formula (a)), D-gulcamine (as represented by Formula (b))



dimethanolamine, diethanolamine, di-n-propanolamine, diisopropanolamine, di(straight or branched)butanolamine (the position of hydroxyl group may vary),

di(straight or branched)pentanolamine (the position of hydroxyl group may vary),  
 di(straight or branched)hexanol amine (the position of hydroxyl group may vary),  
 monohydroxypyrrolidine, monohydroxypyrroline (the position of hydroxyl group  
 may vary), monohydroxypyrrole(the position of hydroxyl group may vary),  
 monohydroxypyrazolidine(the position of hydroxyl group may vary),  
 monohydroxyimidazoline (the position of hydroxyl group may vary),  
 monohydroxypyrazole, monohydroxyimidazolidine (the position of hydroxyl  
 group may vary), monohydroxyimidazoline (the position of hydroxyl group may  
 vary), monohydroxyimidazole (the position of hydroxyl group may vary),  
 monohydroxyfuroxane (the position of hydroxyl group may vary),  
 monohydroxypiperidine (the position of hydroxyl group may vary),  
 monohydroxypiperadine (the position of hydroxyl group may vary),  
 monohydroxymorpholine (the position of hydroxyl group may vary),  
 monohydroxyindoline (the position of hydroxyl group may vary),  
 monohydroxyindole (the position of hydroxyl group may vary),  
 monohydroxyisoindole (the position of hydroxyl group may vary),  
 monohydroxypurine (the position of hydroxyl group may vary),  
 monohydroxycarbazole (the position of hydroxyl group may vary),  
 monohydroxy-  $\beta$  -carboline (the position of hydroxyl group may vary),  
 monohydroxyphenoxazine (the position of hydroxyl group may vary),  
 monohydroxyperimidine (the position of hydroxyl group may vary),  
 dihydroxypyrrolidine, dihydroxypyrroline (the position of hydroxyl group may  
 vary), dihydroxypyrrole (the position of hydroxyl group may vary),  
 dihydroxypyrazolidine (the position of hydroxyl group may vary),  
 dihydroxypyrazoline (the position of hydroxyl group may vary),  
 dihydroxypyrazole (the position of hydroxyl group may vary),  
 dihydroxyimidazolidine (the position of hydroxyl group may vary),



dihydroxyimidazoline (the position of hydroxyl group may vary),  
dihydroxyimidazole (the position of hydroxyl group may vary), dihydroxyfuroxane  
(the position of hydroxyl group may vary), dihydroxypiperidine (the position of  
hydroxyl group may vary), dihydroxypiperadine (the position of hydroxyl group  
may vary), dihydroxymorpholine (the position of hydroxyl group may vary),  
dihydroxyindoline (the position of hydroxyl group may vary), dihydroxyindole (the  
position of hydroxyl group may vary), dihydroxyisindole (the position of hydroxyl  
group may vary), dihydroxypurine (the position of hydroxyl group may vary),  
dihydroxycarbazole (the position of hydroxyl group may vary),  
dihydroxy- $\beta$ -carboline (the position of hydroxyl group may vary),  
dihydroxyphenoxazine (the position of hydroxyl group may vary),  
dihydroxyperimidine (the position of hydroxyl group may vary), trimethanolamine,  
methyldimethanolamine, ethyldimethanolamine, triethanolamine,  
methyldiethanolamine, ethyldiethanolamine, tri-n-propanolamine, methyl-di-n-  
propanolamine, ethyl-di-n-propanolamine, triisopropanolamine,  
methyldiisopropanolamine, ethyldiisopropanolamine,  
tri(straight or branched)butanolamine,  
methyl-di(straight or branched) butanolamine,  
ethyl-di(straight or branched)butanolamine,  
tri(straight or branched)pentanolamine,  
methyl-di(straight or branched)pentanolamine and ethyl-di(straight or  
branched)pentanolamine.

Although not restricted, the ratio of the amine compound of (30a) to the  
chlorine-containing compound of formula (29a) in the reaction is preferably one  
mole or more of amine compound per mole of chlorine-containing compound,  
and more preferably 1 to 20 moles of amine compound per mole of the chlorine-  
containing compound.

The reaction temperature may be in the range of - 20 to 150 °C, preferably - 10 to 80 °C.

The second nitrogen-containing compound of the present invention is a polybutenylamine compound obtained by modifying the terminal ends of a polybutene compound derived from the polymerization of at least one member selected from n-butene, 2-butene and isobutene.

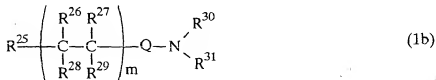
The polymerized portion constituting the polybutenylamine compound according to the present invention may be a homopolymer or copolymer of one or more members selected from n-butene, 2-butene and isobutene. The copolymer may be a random-, alternating- or block copolymer.

Eligible starting materials of the inventive polybutenylamine compound include n-butene, 2-butene and isobutene. Preferred is isobutene, because it provides a gasoline additive with enhanced detergency.

Although the polymerized portion of the polybutenylamine compound according to the present invention is formed by polymerizing a starting material such as n-butene, 2-butene and isobutene, there may be other olefins present such as ethylene and propylene, in the starting material of the reaction.

The polybutenylamine compound may have any of a hydrogen atom, a hydrocarbon group, an oxygen-containing group such as alkanol, and a nitrogen-containing group such as aminoalkyl, bonded to the nitrogen atom of the amine group.

The polybutenylamine compound may be those represented by the formula



In formula (1b), R<sup>25</sup> can be any of n-butyl, sec-butyl or tert-butyl group,

but is preferably tert-butyl, since tert-butyl provides an additive with an enhanced detergency.

$R^{26}$ ,  $R^{27}$ ,  $R^{28}$  and  $R^{29}$  are each independently a hydrogen, a methyl or an ethyl group, selected such that the total number of carbon atoms in groups  $R^{26}$  -  $R^{29}$  is always 2. In other words, the repeating unit in formula (1b) designated as "m" unit, has a structure originating from 1-butene, 2-butene, or isobutene. Variable m is an integer from 1 to 100. When "m" is 1 or greater, the linked repeating units in the number of "m" may be in the form of a homopolymer or a copolymer comprised of one or more of 1-butene, 2-butene, and isobutene. The copolymerization form may be random- or alternating.

However, within the repeating unit, it is preferred that either  $R^{26}$  and  $R^{28}$  are each hydrogen when  $R^{27}$  and  $R^{29}$  are each a methyl group, or  $R^{26}$  and  $R^{28}$  are each a methyl group when  $R^{27}$  and  $R^{29}$  are each hydrogen. These combinations result in gasoline additives with enhanced detergency in a combustion chamber.

In view of maintaining the dispersion properties of gasoline and enhancing the detergency of the resulting additive, m indicating the number of the repeating unit is necessarily 1 or more, preferably 5 or more, more preferably 10 or more, while m is necessarily 100 or less, preferably 50 or less, more preferably 40 or less. Preferred additives in which m is 40 or less result in suppressing the occurrence of valve-stick and the deterioration of thermal decomposition properties, leading to the formation deposits in a combustion chamber, which would otherwise cause the increase of molecular weight.

In formula (1b), Q is a group represented by one of formula (2b) to (7b), but is preferably the group of formula (2b) or (6b), more preferably the group of formula (6b) as additives featuring a group of formula (6b) have excellent detergency.

$R^{30}$  and  $R^{31}$  in formula (1b) are each independently a hydrogen atom, a  $C_1 - C_{10}$  hydrocarbon group, a  $C_1 - C_8$  alkanol group or a group of formula (8b) above.

The  $C_1 - C_{10}$  hydrocarbon group here encompasses  $C_1 - C_{10}$  straight or branched alkyl groups,  $C_2 - C_{10}$  straight or branched alkenyl,  $C_3 - C_{10}$  cycloalkyl or alkylcycloalkyl groups,  $C_6 - C_{10}$  aryl or alkylaryl groups and  $C_7 - C_{10}$  arylalkyl groups.

Specific examples of the  $C_1 - C_{10}$  alkyl group are methyl, ethyl, n-propyl, isobutyl, n-butyl, isobutyl, sec-butyl, tert-butyl, straight or branched pentyl, straight or branched hexyl, straight or branched heptyl, straight or branched octyl, straight or branched nonyl and straight or branched decyl groups.

Specific examples of the  $C_2 - C_{10}$  alkenyl group are ethenyl, n-propenyl, isopropenyl, n-butenyl, isobutenyl, sec-butenyl, tert-butenyl, straight or branched pentenyl, straight or branched hexenyl, straight or branched heptenyl, straight or branched octenyl, straight or branched nonenyl and straight or branched decenyl groups.

Specific examples of the  $C_5 - C_{10}$  cycloalkyl or alkylcycloalkyl group are cyclopentyl, cyclohexyl, cycloheptyl, methylcyclopentyl, dimethylcyclopentyl (inclusive of all positional isomers), ethylcyclopentyl (inclusive of all positional isomers), straight or branched propylcyclopentyl (inclusive of all positional isomers), ethylmethylcyclopentyl (inclusive of all positional isomers), trimethylcyclopentyl (inclusive of all positional isomers), diethylcyclopentyl (inclusive of all positional isomers), ethyldimethylcyclopentyl (inclusive of all positional isomers), straight or branched propylmethylcyclopentyl (inclusive of all positional isomers), straight or branched propylethylcyclopentyl (inclusive of all positional isomers), methylcyclohexyl (inclusive of all positional isomers), dimethylcyclohexyl (inclusive of all positional isomers), ethylcyclohexyl (inclusive

[illegible]

Specific examples of the  $C_7 - C_{10}$  alkylaryl group are benzyl, methylbenzyl (inclusive of all positional isomers), dimethylbenzyl (inclusive of all positional isomers), phenethyl, methylphenethyl (inclusive of all positional isomers) and dimethylphenethyl groups (inclusive of all positional isomers).

- 45 -

branched hydroxyheptyl, straight or branched hydroxyoctyl, straight or branched hydroxynonyl and straight or branched hydroxydecyl groups, among which  $C_1 - C_4$  alkanol groups are preferred.

$R^{30}$  and  $R^{31}$  may be the group of formula (8b). In formula (8b),  $R^{32}$  is a  $C_1 - C_{24}$  alkylene group, such as methylene, ethylene, propylene (1-methylethylene, 2-methylethylene), trimethylene, butylene (1-ethylethylene, 2-ethylethylene), 1,2-dimethylethylene, 2,2-dimethylethylene, 1-methyltrimethylene, 2-methyltrimethylene, 3-methyltrimethylene and tetramethylene. In view of providing the resulting additive with an excellent detergency,  $R^{32}$  is preferably a  $C_1 - C_3$  alkylene group, such as methylene, ethylene, propylene (1-methylethylene, 2-methylethylene) and trimethylene groups.

$R^{33}$  in formula (8b) is hydrogen or a  $C_1 - C_4$  alkyl group. Specific examples of the  $C_1 - C_4$  alkyl group are methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl and tert-butyl. Among these, preferred for  $R^{33}$  are hydrogen and  $C_1 - C_3$  alkyl groups, more preferred are hydrogen, methyl and ethyl groups, and the most preferred is hydrogen.

$R^{34}$  in formula (8b) is hydrogen or a  $C_1 - C_{10}$  hydrocarbon group. The  $C_1 - C_{10}$  hydrocarbon group here encompasses those already exemplified with respect to  $R^{30}$  and  $R^{31}$ . Preferred for  $R^{34}$  are hydrogen or  $C_1 - C_3$  alkyl groups, more preferred are hydrogen, methyl and ethyl groups and the most preferred is hydrogen. An additive which features a preferred  $R^{34}$  group exhibits excellent detergency.

The letter, n, in formula (8) indicates the number of the repeating units in formula (8b), and may be an integer from 1 to 5, but is preferably from 1 to 3, more preferably 1 or 2, and most preferably  $n = 1$ . An additive in which  $n = 1$  provides excellent detergency. If n is 2 or greater, the repeating units may each

have the same or different structure. If the repeating units having different structures are present, they may be random-, alternating- or block-bonded.

$R^{30}$  and  $R^{31}$  in formula (1b) are each preferably hydrogen, a  $C_1 - C_4$  alkanol group, or a group of formula (8b) in view of providing the resulting additive with an excellent detergency.

The number-average molecular weight of a polybutenylamine compound of formula (1b) is not particularly restricted but is preferably 200 or greater, more preferably 400 or greater and even more preferably 700 or greater. Additives having a number-average molecular weight of 700 or greater provide excellent dispersion properties and detergency. In order to suppress valve-stick and the deterioration of thermal decomposition properties, leading to the formation deposits in a combustion chamber, caused by increased molecular weight, the number-average molecular weight of the polybutenylamine of formula (1b) is preferably 6,000 or less, more preferably 3,000 or less and further more preferably 2,400 or less.

The inventive nitrogen-containing compound of formula (1a) or (1b) may be added with other additives to a base gasoline in an amount suitable for a particular application, thereby obtaining a fuel, i.e. a gasoline composition suitable for use in direct injection gasoline engines.

The gasoline composition for use in a direct injection gasoline engine according to the present invention contains the above-described nitrogen-containing compound in an amount of 0.001 to 10 mass percent, based on the total mass of the composition. In order to enhance the detergency in the combustion chamber of a direct injection gasoline engine, particularly the cavity formed on the upper surface of the piston, the lower limit of the content of the nitrogen-containing compound is 0.001 mass percent, preferably 0.003 mass percent, more preferably 0.005 mass percent, even more preferably 0.01 mass

percent, and most preferably 0.015 mass percent. No further enhancement effect can be expected at higher concentrations of additive. The upper limit of the additive content in a gasoline composition is 10 mass percent, preferably 5 mass percent, more preferably 4 mass percent, and most preferably 3 mass percent.

The base gasoline of the above-described gasoline composition may be prepared by blending various gasoline components. Such components may be light naphtha derivable from atmospheric distillation of crude oil, cracked gasoline derivable from catalytic cracking or hydrocracking, reformed gasoline obtainable by catalytic reforming, polymerized gasoline obtainable by olefin polymerization, alkylates derivable from addition reaction or alkylation of a hydrocarbon such as isobutane with a lower olefin, isomerized gasoline derivable from conversion of light naphtha into isoparaffin using an isomerization device, de-n-paraffinized oil, butane, aromatic hydrocarbons and paraffinic fractions derivable from hydrocracking dimerized propylene.

Shown below is a typical blend formulation of an unleaded gasoline which can be used in a direct injection gasoline engine by blending the nitrogen-containing compound according to the present invention.

- (1) reformed gasoline : 0 – 70 vol. %
- (2) light fractions of reformed gasoline  
(boiling at 25 – 120 °C) : 0 – 35 vol. %
- (3) heavy fractions of reformed gasoline  
(boiling at 110 – 200 °C) : 0 – 45 vol. %
- (4) cracked gasoline : 0 – 50 vol. %
- (5) light fractions of cracked gasoline  
(boiling at 25 – 90 °C) : 0 – 45 vol. %
- (6) heavy fractions of cracked gasoline



(boiling at 90 – 200 °C) : 0 – 40 vol. %

- (7) alkylate : 0 – 40 vol. %
- (8) paraffin fraction derived from dimerization and subsequent hydrogenation of propylene : 0 – 30 vol. %
- (9) isomerized gasoline : 0 – 30 vol. %
- (10) MTBE : 0 – 15 vol. %
- (11) light naphtha : 0 – 2- vol. %
- (12) butane : 0 – 10 vol. %

If the benzene content of a gasoline compound needs to be reduced, the reformed gasoline may be added in less amount because it contains more benzene than the other gasoline components. Alternatively, the content of benzene may be reduced by using a reformed gasoline which is reduced in the benzene content by any suitable methods give below:

- (1) removing benzene fraction by distilling a reformed gasoline
- (2) converting benzene into another compound by the following methods (A), (B) and (C),
  - (A) converting benzene by hydrogenating into cyclohexane, methylcyclohexane or the like,
  - (B) converting benzene by reacting it with  $C_9$  or greater aromatic hydrocarbon into toluene, xylene, ethylbenzene or the like
  - (C) alkylating benzene with lower olefins such as ethylene and propylene or with lower alcohols such as methanol and ethanol,
- (4) using a reformer feed of desulfurization heavy naphtha derived from removal of  $C_6$  hydrocarbon by distillation, and
- (5) controlling the operation condition of a catalytic reforming apparatus.

Gasoline additives which can be used in combination with the nitrogen-containing compound according to the present invention include detergent dispersants such as succinimide and polyalkylamine; antioxidants such as phenol- or amine- ones; metal inactivating agents such as Schiff-type compounds and thioamide-type compounds; surface ignition preventers such as organophosphorus-derived compounds; antiicing agents such as polyalcohols and ethers thereof; combustion adjuvants such as alkali metal or alkaline earth metal salts of organic acids and sulfuric esters of higher alcohols; antistatic agents such as anionic surfactants, cationic surfactants and amphoteric surfactants; colorants such as azo dyes; rust inhibitors such as alkenyl succinate; identifying agents such as quinizarin and coumarin, and malodorants such as natural essential-based aromatics.

One or more of these additives may be blended in a gasoline composition in an amount which is preferably less than 0.1 mass percent, based on the total mass of the gasoline composition.

The gasoline composition comprising the inventive gasoline additive, other additives blended as required, and a base gasoline, will preferably exhibit the following distillation properties measured in accordance with JIS K 2254 "Petroleum products-Determination of distillation characteristics"

Running point at 10 vol. % ( $T_{10}$ ) : 35 – 55 °C

Running point at 30 vol. % ( $T_{30}$ ) : 55 – 75 °C

Running point at 50 vol. % ( $T_{50}$ ) : 75 – 100 °C

Running point at 70 vol. % ( $T_{70}$ ) : 100 – 130 °C

Running point at 90 vol. % ( $T_{90}$ ) : 120 – 160 °C

End point : 130 – 210 °C

The lower limit of ( $T_{10}$ ) is 35 °C, preferably 40 °C. A ( $T_{10}$ ) of lower than 30 °C would cause gasoline coking in an injector. The upper limit of ( $T_{10}$ ) is

55 °C, preferably 50 °C, more preferably 48 °C. A (T10) which is higher than 55 °C would lead to decreased low-temperature starting performance of an engine.

The lower limit of ( $T_{30}$ ) is 55 °C, preferably 60 °C. A ( $T_{30}$ ) of lower than 55 °C would invite objectionable high temperature engine performance and cause gasoline coking. The upper limit of ( $T_{30}$ ) is 75 °C, preferably 70 °C, and more preferably 68 °C. A ( $T_{30}$ ) which is higher than 75 °C would lead to aggravated low temperature engine performance.

The lower limit of  $(T_{50})$  is 75 °C, preferably 80 °C. A  $(T_{50})$  of lower than 75 °C would adversely affect low temperature engine performance. The upper limit of  $(T_{50})$  is 100 °C, preferably 95 °C, and more preferably 93 °C. A  $(T_{50})$  which is higher than 100 °C would adversely affect low- and normal-temperature engine performance.

The lower limit of ( $T_{70}$ ) is 100 °C, while the upper limit of ( $T_{70}$ ) is 130 °C, preferably 125 °C, more preferably 123 °C, and most preferably 120 °C. A ( $T_{70}$ ) which is higher than 130 °C would adversely affect low- and normal-temperature engine performance.

The lower limit of ( $T_{90}$ ) is 110 °C, preferably 120 °C. The upper limit of ( $T_{90}$ ) is 160 °C, preferably 150 °C, and more preferably 140 °C. A ( $T_{90}$ ) outside this range would affect low- and normal- temperature engine performance and cause an increase in emission of exhaust gas, the deterioration of engine oil, and the formation of sludge by reducing the level of engine oil diluted by gasoline.

The lower limit of the end point is preferably 130 °C, while the upper limit thereof is 210 °C, preferably 200 °C, more preferably 195 °C, and most preferably 190 °C. An end point which is higher than 210 °C would lead to poor engine performance at normal temperatures.

A gasoline composition containing an inventive gasoline additive should have a vapor pressure which is 70 kPa or less, preferably 65 kPa or less, more preferably 60 kPa or less, and most preferably 55kPa or less, in order to avoid the occurrence of coking and suppress the amount of evaporative emission. The term "vapor pressure" used herein denotes Reid vapor pressure (RVP) measured in accordance with JIS K 2258 "Testing Method for Vapor Pressure of Crude Oil and Petroleum Products (Reid Method)".

The density of the gasoline composition containing the inventive gasoline additive should be within the range of 0.73 to 0.77 g/cm<sup>3</sup>. The lower limit of density is 0.73 g/cm<sup>3</sup>, preferably 0.735 g/cm<sup>3</sup>, as densities less than 0.73 would decrease fuel consumption efficiency. The upper limit of density is 0.77 g/cm<sup>3</sup>, preferably 0.76 g/cm<sup>3</sup>. Density in excess of 0.77 g/cm<sup>3</sup> would lead to insufficient acceleration and spark plug smoldering.

The density used herein denotes a density determined by JIS K 2451 “Testing Method for Densities of Crude Oil and Petroleum Products and Density-Mass-Volume Conversion Table”.

The gasoline composition according to the present invention is substantially free of alkyl lead compounds such as tetraethyl lead. Even though the gasoline composition contains very small amount of such lead compounds, the amount thereof should be held below the lower threshold specified by JIS K 2255 "Petroleum products-Gasoline-Determination of lead content".

The gasoline composition according to the present invention should have a research octane number (RON) which is 89 or greater, preferably 90 or greater, more preferably 90.5 or greater, and most preferably 91 or greater. In order to enhance anti-knocking performance during high-speed driving, the inventive gasoline composition should have a motor octane number (MON) of 80 or greater, preferably 80.5 or greater, and most preferably 81 or greater.

Both RON and MON denote the values measured in accordance with JIS K 2280 "Petroleum products-Fuels-Determination of octane number, cetane number and calculation of cetane index".

The contents of paraffins, olefins and aromatics of the gasoline composition according to the present invention are preferably as follows:

Paraffins (V(P)) : 50 – 100 vol. %

Olefins (V(O)) : 0 – 15 vol. %

Aromatics (V(Ar)) : 0 – 35 vol. %

(V(P)) of the inventive gasoline composition should be in the range of 50 to 100 percent by volume, preferably 60 to 100 percent by volume, and more preferably 70 to 100 percent by volume with the objectives of precluding gasoline coking in an injector, reducing spark plug smoldering and ozone-generation ability of exhaust gas as well as the concentrates of benzene contained therein and avoiding the generation of soot.

V(O) of the inventive gasoline composition should be 0 to 15 percent by volume, preferably 0 to 10 percent by volume, more preferably 0 to 7 percent by volume and most preferably 0 to 5 percent by volume with the objective of precluding gasoline coking in an injector.

V(Ar) of the inventive gasoline composition should be 0 to 35 percent by volume, preferably 0 to 30 percent by volume, more preferably 0 to 25 percent by volume and most preferably 0 to 20 percent by volume with the objective of precluding gasoline coking in an injector, reducing spark plug smoldering and ozone-formability of exhaust gas as well as the concentrates of benzene contained therein, and avoiding the generation of soot.

V(P), V(O) and V(Ar) are the values obtained by the measurement in accordance with JIS K 2536 "Liquid petroleum products-Testing method of components".

The inventive gasoline composition preferably meets the following conditions.

- (1)  $V(\text{Bz})$  : 0 – 1 vol. %
- (2)  $V(\text{Tol})$  : 0 – 30 vol. %
- (3)  $V(\text{C}_8\text{A})$  : 0 – 20 vol. %
- (4)  $V(\text{C}_9\text{A})$  : 0 – 5 vol. %
- (5)  $V(\text{C}_{10}^+\text{A})$  : 0 – 3 vol. %
- (6)  $V(\text{PA}) = 0$  or  
when  $V(\text{PA}) = 0$ ,  $V(\text{MA}) / V(\text{PA}) : 1$  or greater
- (7)  $V(\text{C}_4)$  : 0 – 10 vol. %
- (8)  $V(\text{C}_5)$  : 10 – 35 vol. %
- (9)  $V(\text{C}_6)$  : 10 – 30 vol. %
- (10)  $V(\text{C}_{7+p})$  : 10 – 50 vol. %
- (11)  $V(\text{C}_9+)$  : 0 – 10 vol. %

$V(\text{Bz})$  denotes the amount of benzene, based on the total gasoline composition and should be in the range of 0 to 1 percent by volume, preferably 0 to 0.5 percent by volume. A  $V(\text{Bz})$  which is 0 – 1 volume percent of benzene is contributive to a reduction in the concentration of benzene in the exhaust gas.

$V(\text{Tol})$  and  $V(\text{C}_8\text{A})$  denote the amount of toluene and the amount of a  $\text{C}_8$  aromatic hydrocarbon, respectively, based on the total gasoline composition.  $V(\text{Tol})$  should be 0 to 30 percent by volume, preferably 0 to 20 percent by volume, while  $V(\text{C}_8\text{A})$  should be 0 to 20 percent by volume, preferably 0 to 15 percent by volume. The  $\text{C}_8$  aromatic hydrocarbon may be either ethylbenzene or xylene (including all positional isomers).

$V(\text{C}_9\text{A})$  denotes the amount of a  $\text{C}_9$  aromatic hydrocarbon, based on the total gasoline composition.  $V(\text{C}_9\text{A})$  should be 0 to 5 percent by volume, preferably 0 to 3 percent by volume in order to lower the ozone generation ability

by an exhaust gas. The  $C_9$  aromatic hydrocarbon may be n-propylbenzene, isopropylbenzene (cumene), ethylmethylbenzene (inclusive of all positional isomers) and trimethylbenzene (inclusive of all positional isomers).

$V(C_{10}+A)$  denotes the amount of an aromatic hydrocarbon having 10 or more carbon atoms, based on the total gasoline composition.  $V(C_{10}+A)$  should be 0 to 3 percent by volume, preferably 0 to 1 percent by volume, and more preferably 0 percent by volume in order to lower the ozone generating ability of exhaust gas. The aromatic hydrocarbon having 10 or more carbon atoms may be diethylbenzene (inclusive of all positional isomers), dimethylethylbenzene (inclusive of all positional isomers), tetramethylbenzene (inclusive of all positional isomers) and n-butylmethylbenzene (inclusive of all positional isomers).

$V(MA)$  and  $V(PA)$  denote the amount of an aromatic hydrocarbon having one alkyl substituent (vol. %) and the amount of an aromatic hydrocarbon having more than two alkyl substituents (vol. %), respectively, based on the total gasoline composition. In the present invention, if  $V(PA)$  is 0 or  $V(MA)$  is not 0, the ratio of  $V(MA)$  to  $V(PA)$  should be held to 1 or greater, preferably 1.5 or greater, more preferably 2 or greater.

The above  $V(Bz)$ ,  $V(Tol)$ ,  $V(C_8A)$ ,  $V(C_9A)$ ,  $V(C_{10}+A)$ ,  $V(C_9+)$ ,  $V(MA)$  and  $V(PA)$  are the values determined in accordance with JIS K 2536 "Liquid petroleum products-Testing method of components".

$V(C_4)$  denotes the amount of a  $C_4$  hydrocarbon, based on the total gasoline composition.  $V(C_4)$  is 0 to 10 percent by volume, preferably 0 to 5 percent by volume, and more preferably 0 to 3 percent by volume with the objective of further reducing the amount of evaporative emission. The  $C_4$  hydrocarbon may be any of n-butane, 2-methylbutane (isobutane), 1-butene, 2-butene and 2-methylpropene.

$V(C_5)$  denotes the amount of a  $C_5$  aliphatic hydrocarbon, based on the total gasoline composition. The lower limit of  $V(C_5)$  is 10 percent by volume, and preferably 15 percent by volume. The upper limit of  $V(C_5)$  is 35 percent by volume, and preferably 30 percent by volume. A concentration of 10 percent by volume or more of the  $C_5$  aliphatic hydrocarbon is contributive to the production of a gasoline composition which is capable of providing an excellent engine performance at normal temperature. A concentration of 35 percent by volume or less of the  $C_5$  aliphatic hydrocarbon is contributive to the production of a gasoline composition which is capable of providing an excellent engine performance at high temperature. With the objective of precluding gasoline coking in an injector, it is preferred that the unsaturated hydrocarbon content ( $V(C_5O)$ ) in the  $C_5$  aliphatic hydrocarbon is 0 percent by volume, or that the ratio of the saturated hydrocarbon content to unsaturated hydrocarbon content ( $V(C_5P) / V(C_5O)$ ), should be 1 or greater, preferably 1.5 or greater, more preferably 2 or greater, and most preferably 3 or greater. The  $C_5$  saturated aliphatic hydrocarbon may be n-pentane, 2-methylbutane (isopentane) and 2,2-dimethylpropane (neopentane), while the  $C_5$  unsaturated aliphatic hydrocarbon may be 1-pentene, 2-pentene, 2-methyl-1-butene, 2-methyl-2-butene and 3-methyl-1-butene.

$V(C_6)$  denotes the amount of a  $C_6$  aliphatic acid hydrocarbon, based on the total gasoline composition. The lower limit of  $V(C_6)$  should be 10 percent by volume, preferably 15 percent by volume, while the upper limit of  $V(C_6)$  should be 30 percent by volume, preferably 25 percent by volume. A concentration of 10 percent by volume or greater of  $C_6$  aliphatic acid hydrocarbon is contributive to the production of a gasoline additive which is capable of providing an excellent normal temperature engine performance. A concentration of 30 percent by volume or less of  $C_6$  aliphatic acid hydrocarbon is contributive to the



production of a gasoline additive which is capable of providing an excellent high temperature engine performance. With the objective of precluding gasoline coking in an injector, it is preferred that the unsaturated hydrocarbon content ( $V(C_6O)$ ) in the  $C_6$  aliphatic hydrocarbon should be 0 percent by volume, or that the ratio of the saturated hydrocarbon content to the unsaturated hydrocarbon content ( $V(C_6P) / V(C_6O)$ ), should be 2 or greater, preferably 3 or greater, more preferably 5 or greater, and most preferably 10 or greater.

Specific examples of the  $C_6$  saturated hydrocarbon are n-hexane, 2-methylpentane, 3-methylpentane, 2,2-dimethylbutane and 2,3-dimethylbutane. Specific examples of the  $C_6$  unsaturated hydrocarbon are 1-hexene, 2-hexene, 3-hexene, 2-methyl-1-pentene, 3-methyl-1-pentene, 4-methyl-1-pentene, 2-methyl-2-pentene, 3-methyl-2-pentene, 4-methyl-2-pentene, 2,3-dimethyl-1-butene, 3,3-dimethyl-1-butene and 2,3-dimethyl-2-butene.

$V(C_7+P)$  denotes the amount of a saturated aliphatic hydrocarbon having 7 or more carbon atoms, based on the total gasoline composition. The lower limit of  $V(C_7+P)$  should be 10 percent by volume, preferably 20 percent by volume, while the upper limit of  $V(C_7+P)$  should be 50 percent by volume, and more preferably 45 percent by volume. A  $V(C_7+P)$  which is 10 percent by volume or greater is contributive to the production of a gasoline composition providing an excellent normal temperature engine performance, while a  $V(C_7+P)$  which is 50 percent by volume or less is contributive to the production of a gasoline composition providing an excellent high temperature engine performance. Specific examples of the saturated aliphatic hydrocarbon having 7 or more carbon atoms are n-heptane, 2-methylhexane, 3-methylhexane, 2,2-dimethylpentane, 2,3-dimethylpentane, 2,4-dimethylpentane, 3,3-dimethylpentane, 3-ethylpentane and 2,2,3-trimethylbutane.

$V(C_9+)$  denotes the amount of a hydrocarbon having 9 or more carbon

atoms, based on the total gasoline composition.  $V(C_9+)$  should be in the range of 0 to 10 percent by volume, and preferably 0 to 5 percent by volume. A composition having a  $V(C_9+)$  in this preferred range will provide excellent low- and normal- temperature engine performance and will reduce the amount of gasoline which dilutes engine oil so as to preclude increased amounts of exhaust hydrocarbon, engine oil deterioration, and sludge formation.

The above  $V(C_4)$ ,  $V(C_5)$ ,  $V(C_5P)$ ,  $V(C_5O)$ ,  $V(C_6)$ ,  $V(C_6P)$ ,  $V(C_6O)$ ,  $V(C_7+P)$  and  $V(C_7+P)$  are the values as determined by the following gas chromatography method. These values are measured using a methyl-silicone capillary column 25 to 50 mm in length, a helium or nitrogen carrier gas and an FID detector under the conditions of, 0.5 to 1.5 ml/min in gas flow rate, 1 : 50 to 1 : 250 in partition ratio, 150 to 250 °C in inlet temperature, - 10 to 10 °C in initial column temperature, 200 to 250 °C in end column temperature and 150 to 250 °C in detector temperature.

The gasoline composition according to the present invention may contain oxygen-containing compound in such an amount that the mass percent of oxygen is 0 to 2.7, and preferably 0 to 2.0. The content of oxygen-containing compounds in excess of 2.7 mass percent would lead to an increase in fuel consumption and in NOx emission.

The nitrogen-containing compound described herein encompasses  $C_2 - C_4$  alcohols and  $C_4 - C_8$  ethers. Eligible nitrogen-containing compounds for the inventive gasoline composition include ethanol, methyl-tert-butylether (MTBE), ethyl-tert-butylether, tert-amylethylether (TAME) and tert-amylethylether, among which the preferred are MTBE and TAME, and the most preferred is MTBE. Methanol is not preferred because it is corrosive and would increase the concentration of aldehyde in exhaust gas.

The sulfur content of the inventive gasoline composition should be less

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than 50 mass ppm, preferably 30 mass ppm, more preferably 20 mass ppm, and most preferably 10 mass ppm. The sulfur content if greater than 50 mass ppm would result in poisoning of after-treatment catalysts, increases in the concentration of NO<sub>x</sub>, carbon monoxide, and hydrocarbons, and a sharp rise in benzene emission.

The term "sulfur content" used herein denotes the sulfur content measured in accordance with JIS K 2541 "Crude oil and petroleum products-Determination of sulfur content".

The unwashed existing gum of the inventive gasoline composition should be present in an amount of 20 mg/100ml or less, and the washed gum should be present in an amount of 3 mg/100 ml or less, and preferably 1 mg/100ml or less, as measured in accordance with JIS K2261 "Petroleum products-Motor gasoline and aviation fuels-Determination of existent gum-Jet evaporation method". Deviations from these amounts would lead to the formation of deposits in the fuel-induction system and the occurrence of agglutination in the intake valve.

The gross caloric value of the inventive gasoline composition should be 35,000 J/g or more, preferably 40,000 J/g or more, more preferably 45,000 J/g or more as measured by JIS K 2279 "Crude petroleum and petroleum products-Determination and estimation of heat combustion".

The oxidation stability of the inventive gasoline composition should be over 480 minutes, preferably over 1,440 minutes as measured in accordance with JIS K 2287 "Testing Method for Oxidation Stability of Gasoline (Induction Period Method)". Oxidation stability less than 480 minutes would lead to the formation of gum during storage of the composition.

The inventive gasoline composition should gives a value of 1 or 1a in a copper corrosion test conducted at a temperature of 50 °C for 3 hours in

accordance with JIS K 2513 "Petroleum products-Corrosiveness to copper-Copper strip test". Copper corrosion test values exceeding 1 would indicate that the composition is capable of causing the corrosion of pipes in a fuel system.

The kerosene content of the inventive gasoline composition should be within the range of 0 to 4 percent by volume, based on the total gasoline composition. The term "kerosene content" used herein denotes the content of  $C_{13} - C_{14}$  hydrocarbon (vol. %) based on the total gasoline composition, and is quantitatively determined by a gas chromatographic process in which a methyl-silicone caterpillar column having a column length of 25 to 50 m is fed with a helium or nitrogen gas at a flow rate of 0.5 to 1.5 ml/min. and a divisional ratio of 1 : 50 to 1 : 250 and is operated at an inlet temperature of 150 to 250 °C, an initial column temperature of - 10 to 10 °C, a final column temperature of 150 to 250 °C, and a hydrogen ion detector temperature of 150 to 250 °C.

Examples of the invention will now be provided, with the understanding that the invention is in no way limited by these examples.

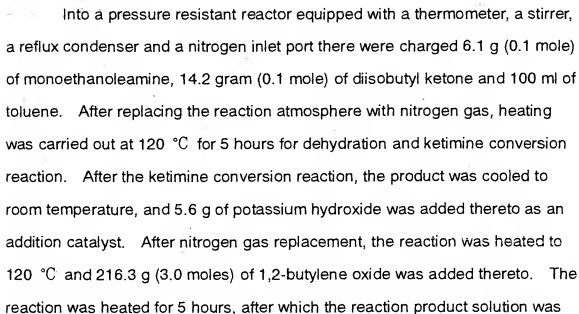
First, synthesis examples of nitrogen-containing compounds included by formula (1a) will be presented.

#### Synthesis Example 1

Into a pressure resistant reactor equipped with a thermometer, a stirrer, a reflux condenser and a nitrogen inlet port there were charged 6.1 g (0.1 mole) of monoethanolamine, 10 g (0.1 mole) of methyl isobutyl ketone and 100 ml of toluene. After filling the reactor atmosphere with nitrogen, heating was carried out at 120 °C for 5 hours for dehydration and ketimine conversion reaction. After the ketimine conversion reaction, the product was cooled to room temperature, and 5.6 g of potassium hydroxide was added thereto as an addition catalyst. The reactor atmosphere was filled with nitrogen gas and then the

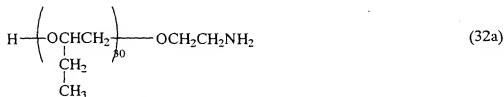
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### Synthesis Example 2



neutralized with acid and filtered to remove the addition catalyst. After adding 5 g of water, the hydrolysis reaction was conducted at 90 °C for 3 hours. The excess water, toluene and ketone were removed from the hydrolysis reaction to obtain 105 g of the target nitrogen-containing compound.

The nitrogen-containing compound was a light yellow oily liquid with a number-average molecular weight of about 2,000. As a result of <sup>13</sup>C-NMR analysis, the nitrogen-containing compound was found to be a polymer with an average structure represented by formula (32a). This will be referred to in the Examples as Compound 2.

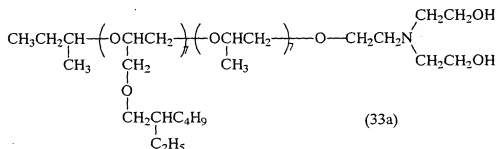


### Synthesis Example 3

Into a pressure resistant reactor equipped with a thermometer, a stirrer, a reflux condenser and a nitrogen inlet port there were charged 6.1 g (0.1 mole) of monoethanolamine, 10 g (0.1 mole) of methyl isobutyl ketone and 100 ml of toluene. After replacing the reactor atmosphere with nitrogen gas, heating was carried out at 120 °C for 5 hours for dehydration and ketimine conversion reaction. After the ketimine conversion reaction, the product was cooled to room temperature, and 5.6 g of potassium hydroxide was added thereto as an addition catalyst. After nitrogen gas replacement, the reaction was heated to 120 °C and 40.6 g (0.7 mole) of propylene oxide and 130.4 g (0.7 mole) of 2-ethylhexyl glycidyl ether were added thereto. The reaction was heated for 5 hours. After adding 9.3 g (0.1 mole) of 2-chlorobutane, the reaction was heated for an additional 2 hours. The reaction product solution was purified and filtered to remove the addition catalyst. After adding 5 g of water, the hydrolysis reaction was conducted at 90 °C for 3 hours. The excess water, toluene and

ketone were then removed and 8.8 g (0.2 mole) of ethylene oxide was added to obtain 160 g of the target nitrogen-containing compound.

The nitrogen-containing compound was a light yellow oily liquid with a number-average molecular weight of about 1,900. As a result of  $^{13}\text{C}$ -NMR analysis, the nitrogen-containing compound was found to be a random copolymer with an average structure represented by formula (33a). This will be referred to in the Examples as Compound 3.

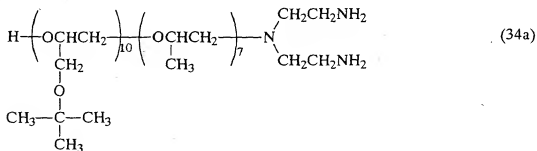


#### Synthesis Example 4

Into a pressure resistant reactor equipped with a thermometer, a stirrer, a reflux condenser and a nitrogen inlet port there were charged 10.3 g (0.1 mole) of diethylenetriamine, 28.4 g (0.2 mole) of diisobutyl ketone and 100 ml of toluene. After replacing the reactor atmosphere with nitrogen gas, heating was carried out at 120 °C for 5 hours for dehydration and ketimine conversion reaction. After the ketimine conversion reaction, the product was cooled to room temperature, and 5.6 g of potassium hydroxide was added thereto as an addition catalyst. After nitrogen gas replacement, the reaction was heated to 120 °C and 40.6 g (0.7 mole) of propylene oxide and 130.2 g (1.0 mole) of tert-butyl glycidyl ether were added thereto. The reaction was heated for 5 hours, after which the reaction product solution was neutralized with acid and filtered to remove the addition catalyst. After adding 5 g of water, the hydrolysis reaction was conducted at 90 °C for 3 hours. The excess water, toluene and ketone were removed from the hydrolysis reaction to obtain 165 g of the target

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CH<sub>3</sub>CH<sub>2</sub>NH<sub>2</sub>

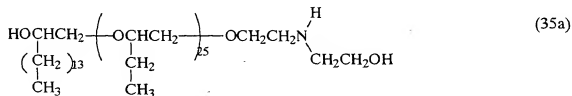


### Synthesis Example 5



nitrogen-containing compound.

The nitrogen-containing compound was a yellow oily liquid with a number-average molecular weight of about 2,150. As a result of  $^{13}\text{C}$ -NMR analysis, the nitrogen-containing compound was found to be a polymer with an average structure represented by formula (35a). This will be referred to in the Examples as Compound 5.



#### Synthesis Example 6

After placing 4.45 g (0.06 mole) of tert-butanol and 3.37 g (0.06 mole) of potassium hydroxide in a 1-liter volume autoclave and replacing the system atmosphere with nitrogen gas, heating was carried out at 90 °C. To the reaction was added 100 ml of toluene, 67.1 g (0.36 mole) of 1,2-ethylhexyl glycidyl ether and 62.7 g (1.08 mole) of propylene oxide, and the reaction was carried out for 5 hours at a reaction temperature of 120 °C. After completion of the reaction, the reaction product solution was neutralized with hydrochloric acid, extracted with toluene, and the toluene was removed by distillation to yield 120 g of a polyoxyalkylene compound.

Next, 8.0 g (0.081 mole) of liquid phosgene was added to a mixed solution of 84.4 g (corresponding to 0.04 mole : calculated from weight-average molecular weight) of the polyoxyalkylene compound and 100 ml of toluene at 0 °C. The reaction was conducted at room temperature for 12 hours while cooling the reflux tube with dry ice. After completion of the reaction, the excess phosgene was removed and the toluene solvent was distilled off to obtain 88 g of a chlorine-containing compound.

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### Synthesis Example 7

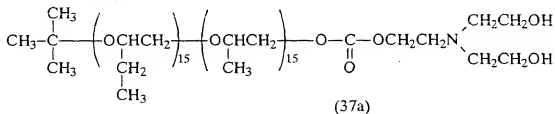
After placing 4.45 g (0.06 mole) of tert-butanol and 3.37 g (0.06 mole) of potassium hydroxide in a 1-liter volume autoclave and replacing the system atmosphere with nitrogen gas, heating was carried out at 90 °C. To the reaction was added 100 ml of toluene, 64.9 g (0.90 mole) of 1,2-butylene oxide and 52.2 g (0.90 mole) of propylene oxide, and the reaction was carried out for 5 hours at a reaction temperature of 120 °C. After completion of the reaction, the

reaction product solution was neutralized with hydrochloric acid, extracted with toluene, and the toluene was removed by distillation to yield 108 g of a polyoxyalkylene compound.

Next, 8.0 g (0.081 mole) of liquid phosgene was added to a mixed solution of 81.0 g (corresponding to 0.04 mole : calculated from the weight-average molecular weight) of the polyoxyalkylene compound and 100 ml of toluene at 0 °C. The reaction was conducted at room temperature for 12 hours while cooling the reflux tube with dry ice. After completion of the reaction, the excess phosgene was removed and the toluene solvent was distilled off to obtain 76 g of a chlorine-containing compound.

Next, 73.1 g (corresponding to 0.035 mole : calculated from weight-average molecular weight) of the chlorine-containing compound was added dropwise to a cooled mixed solution of 100 ml of toluene, 100 ml of pyridine and 59.6 g (0.4 mole) of triethanolamine at 5 °C. The reaction was conducted for 3 hours while keeping the system at 5 °C, after which the reaction was continued at room temperature for 2 hours. After completion of the reaction, the unreacted triethanolamine, produced hydrochloride and toluene solvent were removed, and purification yielded 68 g of the target nitrogen-containing compound.

The nitrogen-containing compound was a dark orange oily liquid with a number-average molecular weight of about 2,200. As a result of <sup>13</sup>C-NMR analysis, the nitrogen-containing compound was found to be a random copolymer with an average structure represented by formula (37a). This will be referred to in the Examples as Compound 7.



### Synthesis Example 8

After placing 3.37 g (0.06 mole) of potassium hydroxide in a 1-liter volume autoclave and replacing the system atmosphere with nitrogen gas, heating was carried out at 90 °C. To the reaction was added 100 ml of toluene and 129.8 g (1.80 mole) of 1,2-butylene oxide temperature of 120 °C. After completion of the reaction, the reaction product solution was neutralized with hydrochloric acid, extracted with toluene, and the toluene was removed by distillation to yield 115 g of a polyoxyalkylene compound.

Next, 8.0 g (0.081 mole ) of liquid phosgene was added to a mixed solution of 87.3 g (corresponding to 0.04 mole : calculated from the weight-average molecular weight) of the polyoxyalkylene compound and 100 ml of toluene at 0 °C. The reaction was conducted at room temperature for 12 hours while cooling the reflux tube with dry ice. After completion of the reaction, the excess phosgene was removed and the toluene solvent was distilled off to obtain 80 g of a chlorine-containing compound.

Next, 78.5 g (corresponding to 0.035 mole : calculated from weight-average molecular weight) of the chlorine-containing compound was added dropwise to a cooled mixed solution of 100 ml of toluene, 100 ml of pyridine and 34.8 g (0.4 mole) of morpholine at 5 °C. The reaction was conducted for 3 hours while keeping the system at 5 °C and was continued at room temperature for 2 hours. After completion of the reaction, the unreacted morpholine, the produced hydrochloride and the toluene solvent were removed, and purification yielded 73 g of the target nitrogen-containing compound.

The nitrogen-containing compound was a dark orange oily liquid with a number average molecular weight of about 2,300. As a result of <sup>13</sup>C-NMR analysis, the nitrogen-containing compound was found to be a polymer with an

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$$\text{H}-\left(\text{OCHCH}_2\right)_{30}-\text{O}-\text{C}(=\text{O})-\text{N}\begin{array}{c} \diagup \diagdown \\ \diagdown \diagup \end{array} \text{O} \quad (38a)$$

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Table 1

	Composition (mass %)		Engine Evaluation Test Results				THC (g/km)	Smoke (%)
	Base Gasoline	Nitrogen- Containing Compound	Deposits (mg)					
			Cavity (inside)	Cavity (outside)	Cylinder Head			
Example 1	[99.98]	Compound 1 [0.02]	124	565	825	0.11	4.0	
Example 2	[99.98]	Compound 2 [0.02]	138	580	837	0.11	4.6	
Example 3	[99.98]	Compound 3 [0.02]	109	493	798	0.10	4.3	
Example 4	[99.98]	Compound 4 [0.02]	98	524	763	0.09	3.9	
Example 5	[99.98]	Compound 5 [0.02]	133	559	857	0.12	4.6	
Example 6	[99.98]	Compound 6 [0.02]	144	578	864	0.13	4.8	
Example 7	[99.98]	Compound 7 [0.02]	156	598	870	0.14	5.4	
Example 8	[99.98]	Compound 8 [0.02]	149	553	843	0.13	5.2	
Example 9	[99.98]	Compound 9 [0.02]	158	583	854	0.12	4.8	
Example 10	[99.98]	Compound 10 [0.02]	197	604	886	0.13	5.1	
Example 11	[99.98]	Compound 11 [0.02]	202	615	870	0.13	5.2	
Comparative Example 1	[100]	—	504	836	1282	0.18	10.4	

As clearly shown by the engine evaluation test results in Table 1, the gasoline compositions of Examples 1 to 11 according to the invention were all capable of reducing combustion chamber deposits in direct injection gasoline engines. The reduction in deposits was particularly notable in the cavity directly which directly contacts fuel during stratified combustion. In addition, the increase in THC and smoke volume, believed to result from loss of control due to fuel adhesion by chamber deposits, was successfully inhibited.